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**INTERCOMPARISON OF METHODS
FOR THE MEASUREMENT OF
CARBONACEOUS AEROSOL SPECIES**

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ABSTRACT

A field study was performed evaluating methods for the measurement of carbonaceous atmospheric aerosols. The sampling techniques assessed included a proposed fine particulate carbon sampler operating for 12-hour sampling periods, and two tandem filter samplers operating at face velocities of 47 and 10 cm/sec, respectively, for 4 or 8-hr periods. Samples were analyzed for elemental or black carbon with a light absorption technique, and for total carbon and carbonate carbon with a coulometric detector. Organic carbon was estimated by difference. Samplers were operated at Citrus College, Glendora, CA during the period Aug. 12 - Aug. 20, 1986 in parallel with samplers operated by other investigators.

The proposed fine particulate carbon sampler consisted of a cyclone, parallel plate diffusion denuder packed with coarse, activated alumina, and a quartz fiber filter followed by a fluidized bed of activated alumina. The denuder was intended to prevent sorption of vapor-phase carbonaceous material on the quartz filter, particulate matter thereon, or the fluidized bed. The fluidized bed was intended to trap carbonaceous material lost from the filter by volatilization following collection in the particulate state.

Based on QA studies as well as atmospheric particulate sample results, the alumina denuder was judged ineffective in eliminating the positive error in organic aerosol sampling with quartz filters. The results indicate that compounds not retained efficiently on alumina are being sorbed by quartz filters to produce a positive artifact in carbonaceous aerosol sampling. The contrast in denuder effectiveness between the present trials and our earlier studies is discussed. The failure of the denuder in the present work also prevents interpretation of carbon recoveries on the fluidized bed of Al_2O_3 regarding the significance of volatilization of particulate carbon from a quartz filter sampler.

Comparing particulate organic carbon results as a function of prefilter face velocity, measured airborne concentrations were about 50% higher at 10 cm/sec compared to 47 cm/sec. With tandem filter samplers, after-filter C was about 20% of the total recovered carbon at both 10 and 47 cm/sec. Expressed in $\mu\text{g}/\text{m}^3$, after-filter results at 10 cm/sec were about twice the level at 47 cm/sec, consistent with greater efficiency for sorption of vapor-phase organic compounds at lower face velocity. Subtracting the after-filter carbon results from the organic carbon (i.e. particle plus sorbed vapor phase carbon) measured on the prefilter did not greatly improve the agreement in organic carbon concentrations measured with the prefilters of the samplers at the two face velocities. Thus, neither measurement of particulate organic carbon can be considered accurate.

AIHL carbon analyses of atmospheric particulate samples were compared to those by S. Cadle, General Motors Research Laboratory. The total carbon and organic carbon data sets for the two laboratories were highly correlated ($r > 0.94$). AIHL total carbon results averaged 4% lower; organic carbon averaged 15% higher, and elemental carbon averaged 17% lower than those by GM.

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Black carbon standards used to calibrate the laser transmission method were provided by L. Gundel, Lawrence Berkeley Laboratory. Quality assurance for this program was greatly benefited by discussions with S. Hering and P. McMurry. R. Countess and S. Cadle provided results of their analyses of round-robin carbon samples.

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I. SUMMARY AND CONCLUSIONS

A field study was performed evaluating sampling and analytical methods for the measurement of carbonaceous atmospheric aerosols. A proposed fine particulate carbon sampler operating for 12-hour periods and two, tandem filter samplers at face velocities of 47 and 10 cm/sec, respectively, for 4 or 8-hr periods were evaluated. Samples were analyzed for elemental or black carbon with a light absorption technique, and, for total carbon and carbonate carbon, with a coulometric detector after conversion to CO_2 .

Samplers were operated at Citrus College, Glendora, CA during the period Aug. 12 - Aug. 20, 1986 in parallel with samplers operated by other investigators. Comparison of the present results with those from other groups is beyond the scope of the present contract. However, analytical results for "round robin" samples are compared to those from another participating laboratory.

The proposed fine particulate carbon (FPC) sampler consisted of a cyclone, parallel plate diffusion denuder packed with coarse, activated alumina, and a quartz fiber filter followed by a fluidized bed of activated alumina. The filter medium in all samplers was prefired Pallflex 2500 QAO quartz fiber. The cyclone excluded particles $>2.8 \mu\text{m}$. The denuder was intended to prevent sorption of vapor-phase carbonaceous material on the quartz filter, particulate matter thereon, or on the fluidized bed. The fluidized bed was intended to trap carbonaceous material lost from the filter by volatilization following collection in the particulate state. If the denuder were effective, the sum of the carbon recovered from the filter plus fluidized bed would provide a measure of fine particulate carbon. Laboratory studies with model compounds provided support for this approach.

The FPC sampler was operated in parallel with a second unit identical except for the absence of the denuder. This is referred to herein as a proposed low volatility fine carbon (LVFC) sampler since it was intended to retain both particulate matter and some vapor phase material. The difference in carbon recovered from the FPC and LVFC samplers provided a measure of the carbon removed by the denuder.

In addition to ambient aerosol sampling, QA studies at the field site and in the laboratory assessed the effectiveness of the denuder and the sorption properties of quartz filters for vapor phase carbonaceous material in ambient air. This was done by employing quartz fiber pre-filters ahead of the FPC and LVFC samplers. Accordingly, only vapor phase carbon could enter the sampler. If the denuder were effective for the removal of the carbonaceous material able to be sorbed on the sampling media, then no carbon should be recovered from the filter and alumina in these trials. For one 12-hour period at Citrus College, with the denuder present the total recovered carbon was reduced by only 32% relative to that without the denuder. Most of the reduction occurred in carbon retained on the fluidized bed; low polarity carbonaceous material was reduced by 70% and polar organic compounds, by an even greater percentage. By contrast, carbon recovered from the quartz filter was only reduced by 12%. Thus the denuder appeared to be ineffective in

eliminating the positive error in organic aerosol sampling with quartz filters. Subsequent laboratory ambient air trials showed similar trends. A program, under sponsorship of the Electric Power Research Institute, is continuing in our laboratory to develop a denuder with sorption properties matched to atmospheric requirements.

Based on the QA studies described above, atmospheric aerosol results with the proposed FPC and LVFC samplers at Citrus College could not be expected to provide an improved measure of carbon-containing aerosols. For eighteen, 12-hr sampling periods, results paralleled those described above using pre-filters ahead of both samplers; the carbon recovered from the alumina was less than one third that on the filter preceding it. Comparison of total organic carbon on the two samplers showed little, if any, difference. Thus the aerosol sampling results are consistent with the QA findings, viz., that the denuder was ineffective in eliminating the positive error in organic aerosol sampling.

Failure of the FPC sampler to function as intended is traceable to the initial assumption, viz., that the positive artifact in filter sampling relates to the retention of the vapor phase fraction of relatively low vapor pressure materials (e.g. materials which can exist in either particulate or vapor phases under atmospheric conditions). Alumina retains such materials efficiently, but is unable to retain efficiently more volatile vapor phase materials. Therefore, the positive artifact observed with quartz filters in the proposed FPC sampler implies that these more volatile materials can be partially retained on quartz fiber filters. Consequently, no conclusions are possible from the present data regarding the relative magnitudes of the positive and negative sampling artifacts for particulate carbonaceous material.

The present findings make clear the need for characterization of the volatility and polarity of the vapor phase atmospheric compounds sorbed on quartz filters, and studies of collection efficiencies with more suitable sorbent materials, followed by further field trials.

Comparing organic carbon results as a function of filter face velocity, measured airborne concentrations were about 50% higher at 10 compared to 47 cm/sec results. With tandem filter samplers, after-filter C was about 20% of the total recovered carbon at both 10 and 47 cm/sec. Expressed in $\mu\text{g}/\text{m}^3$, after-filter results at 10 cm/sec were about twice the level at 47 cm/sec suggesting greater efficiency for sorption of vapor-phase organic compounds at lower face velocity. If it is assumed that volatilization of previously collected carbon is a negligible contributor to the carbon collected on the after-filter, a measure of particle phase organic carbon on the quartz prefilter can be obtained by subtracting the after-filter carbon results from the particle plus sorbed, vapor phase organic carbon measured on the prefilter. However, for the present study, such subtraction did not improve greatly the agreement in organic carbon concentrations measured with the prefilters of the samplers at the two face velocities. Thus, neither measurement of particulate organic carbon can be considered an accurate measure of this parameter. Furthermore, this suggests that use of an additional tandem sampler with a Teflon prefilter and quartz after-filter is needed to minimize removal of vapor phase carbon by the prefilter, and provide

a better estimate of vapor phase carbon sorbed on a quartz prefilter. Such a strategy has been employed elsewhere (13).

AIHL carbon analyses of atmospheric particulate samples were compared to those by S. Cadle, General Motors Research Laboratory. The total carbon and organic carbon data sets for the two laboratories were highly correlated ($r > 0.94$), AIHL total carbon results averaged 4% lower; organic carbon averaged 15% higher, and elemental carbon averaged 17% lower than those by GM. The AIHL elemental carbon values averaged only half those by GM for the auto exhaust and woodsmoke samples. Charring of auto exhaust and wood smoke samples during the pyrolytic GM analysis may contribute to the greater difference in results with these samples.

II. INTRODUCTION

A. Review of Prior Studies Using Denuder Techniques

In a preceding ARB-sponsored research program, a technique for the sampling of carbonaceous particle-phase materials was proposed and evaluated to a limited degree (1, 2). The technique was intended to minimize both positive and negative sampling errors. It employed a diffusion denuder, a filter and a fluidized bed of sorbent (Figure 1). The denuder was intended to discriminate between gaseous and particulate carbonaceous material. Particles, due to their low diffusion coefficient, should pass through the denuder (residence time ca. 1.3 sec), while gaseous organics of relatively low vapor pressure are retained on the denuder wall coating. In the ARB programs this was 40-200 mesh Al_2O_3 on an adhesive composed of silicone stopcock grease and rubber cement. Particles are retained on a quartz filter, while the carbon volatilized from the particles is intended to be retained by sorption on the filter medium and on the fluidized bed. We refer to this as a proposed particulate carbon (PC) sampler.

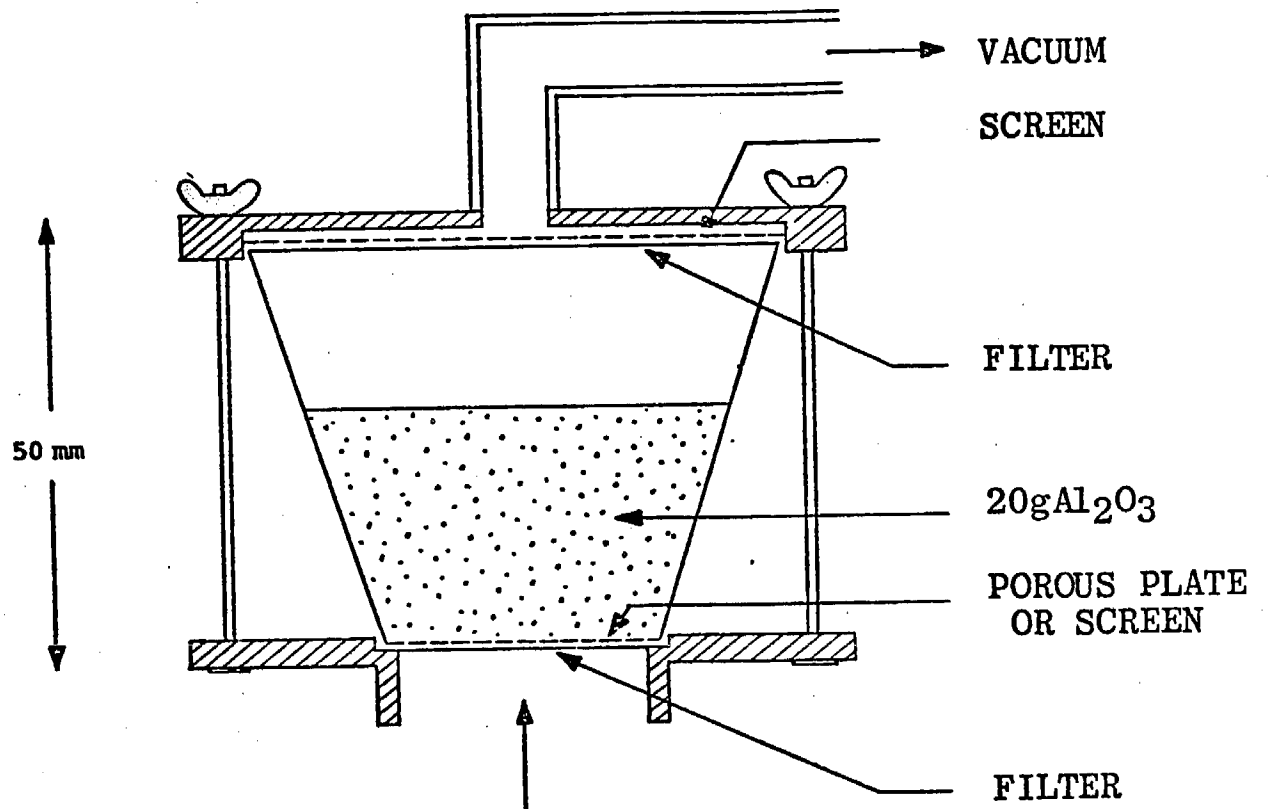
This approach is predicated on the assumption that the vapor-phase atmospheric carbonaceous materials able to be retained by sorption on a quartz filter and/or the particulate matter thereon are strongly bound on contact with activated alumina. The technique to measure particulate carbonaceous material is subject to positive errors if vapor-phase organic compounds not retained by the denuder, are retained (and subsequently recovered from) the filter and/or the fluidized bed.

If the proposed PC sampler is altered by removing the denuder, the carbon retained by the filter and fluidized bed should include some of the initially gas phase, low vapor pressure organic compounds as well as particle phase carbon. Accordingly, we refer to the PC sampler without the denuder as a proposed low volatility carbon (LVC) sampler. If the efficiency of the fluidized beds are equal for the two samplers, then the difference in carbon retained by the LVC and PC samplers is an upper limit estimate of the positive artifact possible in sampling carbonaceous aerosol with filter media for the same location and time interval.

The presence of a denuder ahead of the filter plus alumina in the PC sampler can influence the carbon recovered from a following filter by decreasing the potential positive artifact caused by retention of gas phase organics on the denuder. It can enhance the negative artifact for carbon recovered from the filter by enhancing volatilization of a species whose vapor-phase component has been sharply diminished in concentration. If such volatilized compounds are recaptured on the fluidized bed of alumina, this is of no significance. It can enhance the recovery of carbon from the alumina by serving to dehydrate the incoming sample air, and, therefore, increase the sampling efficiency, since the efficiency of alumina for carbonaceous material decreases with increased

Figure 1.

Fluidized Bed Sampler



moisture content. Finally, it can enhance the recovery of carbon on the filter if carbon-containing alumina dust particles are transferred from the denuder to the filter.

Use of an inorganic sorbent permits quantitation of atmospheric carbonaceous materials using total carbon analytical methods, following solvent extraction and evaporation of solvent. Loss of sample during solvent removal must be minimized.

In a study currently in progress, sponsored by the Electric Power Research Institute, this approach to particulate carbon sampling is being further evaluated using model compounds. As a result of this work, a modified PC sampler was constructed. In place of a parallel tube denuder, in which Al_2O_3 was dusted on adhesive-coated tubes, a parallel plate denuder was constructed in which the air sample passes through three or four parallel channels, each surrounded by 7 to 12 mesh Al_2O_3 beads (Figure 2). Following the denuder is a fluidized bed sampler, modified to permit operation at 20 Lpm rather than 9.5 Lpm (Figure 3).

The performance of the higher flow rate sampler components with model compounds is illustrated in Tables 1 and 2. With four parallel channels, the denuder exhibited 93% efficiency for octadecane vapor (C-18), and 98% for dibutylphthalate vapor (DBP). With C-18 vapor, the fluidized bed sampler efficiency was 97 to 99% depending on the water content of the alumina. Higher vapor pressure organic compounds (benzoic acid and resorcinol) showed much lower retention. These materials are expected to exist principally in the gas phase in the atmosphere.

The face velocity of the filter used in the fluidized bed sampler (Figure 3) was 37 cm/sec. Previous studies suggested that the degree of retention of atmospheric carbonaceous material can increase with decreasing face velocity (Figure 4) in the range 10 to 50 cm/sec (1,2). A possible cause of this behavior is the enhanced volatilization of organic compounds at higher face velocities (and correspondingly higher pressure drops across the filter). Alternatively, sorption of gas phase carbonaceous materials might be enhanced at lower face velocity.

Our preceding studies also included development and evaluation of methodology for the quantitation of elemental and organic carbon in air particulate matter samples (3,4). The methodology evolved from this work employed light absorption and reflectance methods for elemental carbon, and total carbon analysis by combustion to CO_2 and quantitation of CO_2 by thermal conductivity detector GC or with a coulometer. Organic carbon was calculated as the difference between total carbon and elemental carbon, since, for urban samples collected in the South Coast Air Basin, carbonate C has previously been shown to be a negligible contributor (2).

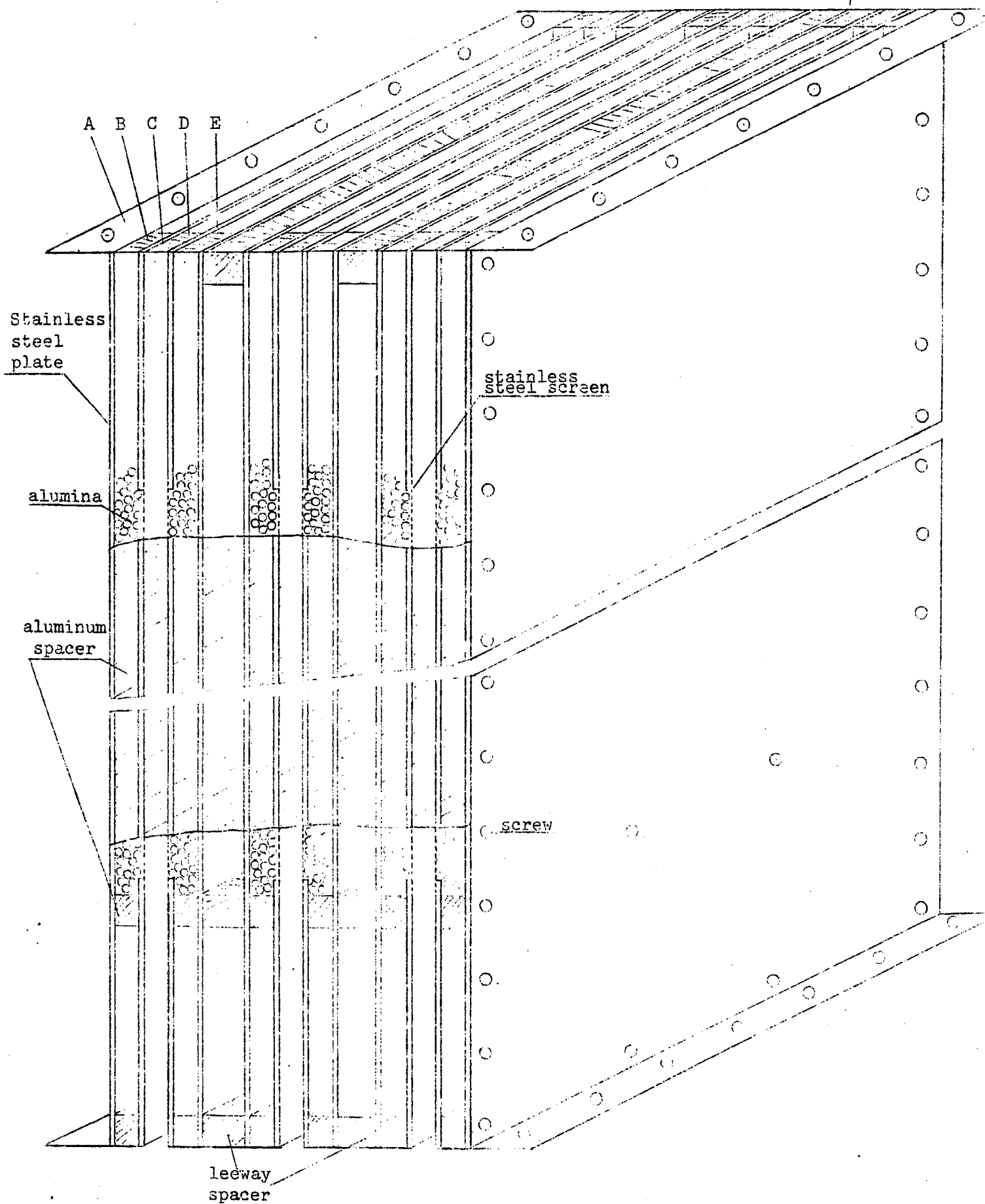


Figure 2.

PARALLEL PLATE DENUDER

Figure 3. The 20 LPM Fluidized Bed Sampler

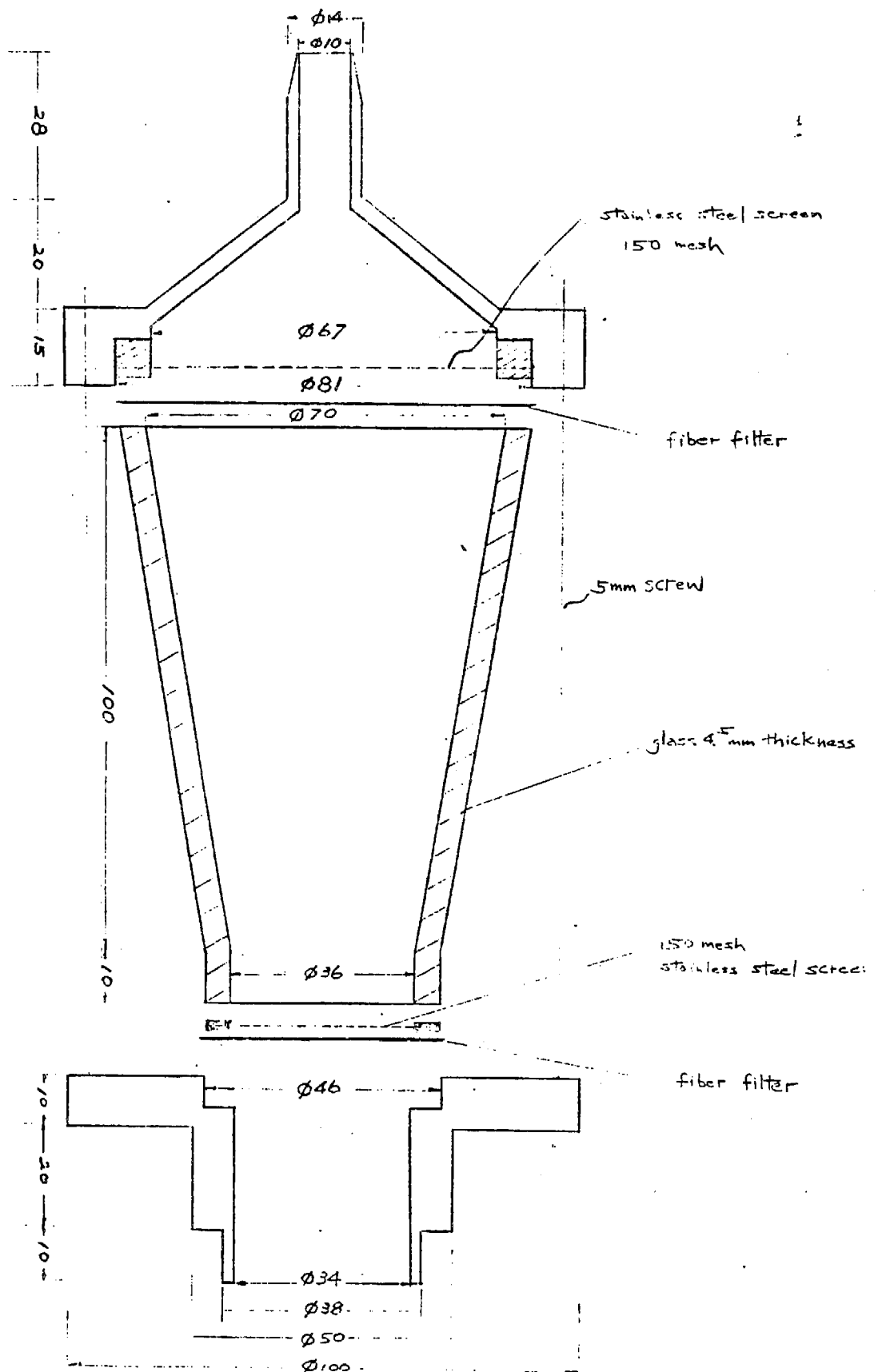


Table 1. Efficiency of High Flow Rate Fluidized Bed Sampler with Al₂O₃

<u>Vapor Sample</u>	<u>Flow Rate (Lpm)</u>	<u>Temp. (°C)</u>	<u>R.H. (%)</u>	<u>Vapor Concentration (µg/m³)</u>	<u>Dosage (µg)</u>	<u>Efficiency (%)</u>
octadecane	18.4	18.8	66	545	1205	99.2 ± 0.04
octadecane + 4% H ₂ O	20.0	20	68	426	512	96.7
benzoic acid	20.0	19.6	50.5	375	900	66.0 ± 1.3
resorcinol	20.0	19.6	75.3	11	66	63.6 ± 0.6

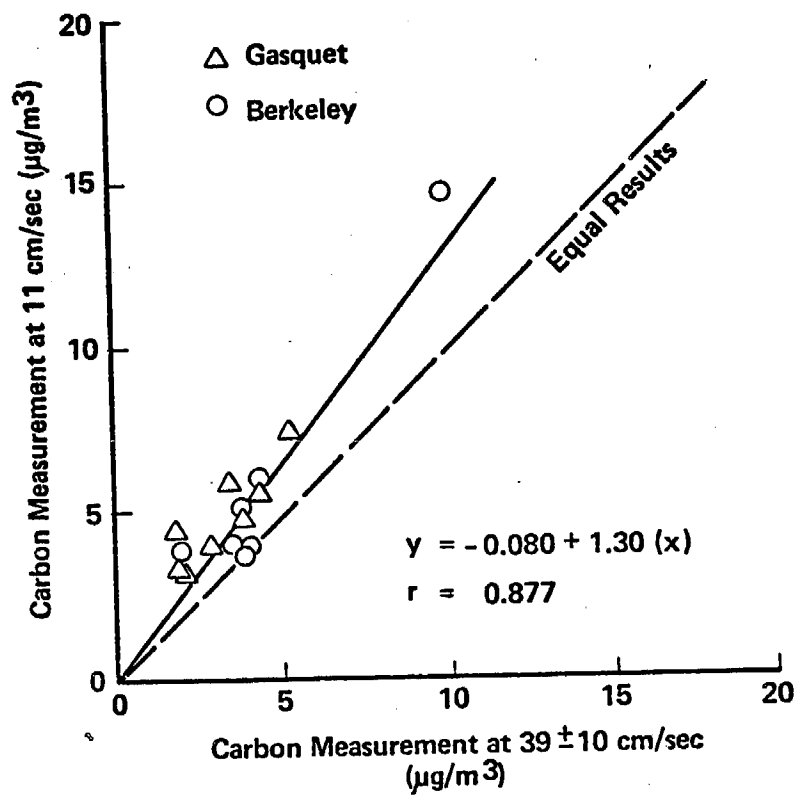
Table 2. Efficiency of Parallel Plate Al_2O_3 Denuder for Model Compound Removal at 20 Lpm

<u>Vapor Source</u>	<u>No. of Channels</u>	<u>Time, Hours</u>	<u>Temp. ($^{\circ}\text{C}$)</u>	<u>R.H. (%)</u>	<u>Vapor Concentration ($\mu\text{g}/\text{m}^3$)</u>	<u>Efficiency (%)</u>
C-18	3	2	20.4	64	251	86.3 ± 0.5
C-18	4	2	20.5	63	344	94.6 ± 0.2
C-18	4	2	19.5	68	296	91.6 ± 1.0
DBP	3	16.7	20.0	70	43.5	97.7 ± 0.2

a. Results shown for individual trials.

Figure 4.

The Influence of Sampling Face Velocity
on Recovered Carbon Concentrations



B. Prior Studies Using Tandem Filters

Several prior studies have sampled carbonaceous particulate matter with two filters in tandem (5-7). With two quartz filters in tandem, the carbon recovered from the after-filter typically represented 10-15% of the total. Such carbon represents the sum of that sorbed from initially gaseous material plus the carbon volatilized from the prefilter and re-adsorbed on the after-filter. Cadle et al. (5) noted that relatively little carbon could be volatilized from the loaded prefilter in clean air following atmospheric sampling. They concluded that sorption of initially gaseous carbon dominated over volatilization as a source of error during sampling. J. Huntzicker et al. (7) assessed particulate carbon sampling with tandem filters consisting of quartz-quartz and Teflon-quartz filter combinations at varying face velocities. Conclusions from their work were:

1. The apparent concentration of aerosol organic carbon on quartz filters decreased with increasing filter face velocity.
2. The concentration of organic carbon on backup filters also decreased with increasing face velocity.
3. At a face velocity of 40 cm/sec, the concentration of organic carbon on quartz fiber backup filters behind Teflon front filters was about a factor of 2 greater than on quartz filters behind quartz prefilters.
4. Subtracting the concentrations of organic carbon on quartz after-filters behind Teflon prefilters from organic carbon values on quartz prefilters greatly removed the face velocity dependence of the apparent particulate organic carbon concentrations and provided an improved estimate of the true aerosol organic carbon concentration.

Huntzicker et al. concluded that face-velocity dependent sorption of vapor phase materials predominates over volatilization in influencing organic aerosol sampling errors.

C. Objectives of the Current Work

The intent of the current work was to compare sampling techniques for atmospheric carbonaceous aerosols, sampling in parallel with a number of other research groups. A comparison of experimental results with other research groups is beyond the scope of the present work. However, the present report evaluates the degree of agreement between our samplers and interprets the results as regards sampling and analytical errors. Analytical results for total, organic and elemental carbon are compared to those by another laboratory.

The specific objectives of this work are as follows:

1. To sample in parallel with (a) a proposed fine particle carbon sampler, (b) a sampler intended to collect both such particulate carbon and low vapor pressure, vapor phase materials, and (c) conventional filter samplers for carbonaceous aerosol.
2. To compare carbonaceous aerosol sampling with filters at relatively high and low face velocities.
3. To assess the degree of sorption of initially gas phase carbonaceous materials on quartz filters by sampling with such filters in tandem at both high and low face velocities.
4. To provide analyses for total carbon, elemental and organic carbon useful for interlaboratory comparisons of results.
5. To prepare a final report summarizing all results.

III. EXPERIMENTAL

A. Description of Samplers

Table 3A summarizes the sampling scheme, employing four parallel samplers:

1. A proposed fine particulate carbon (FPC) sampler at 20 Lpm using a Teflon-coated cyclone (8) to exclude particles $>3 \mu\text{m}$, a four-channel parallel plate denuder and a fluidized bed sampler. The denuder is oriented vertically, with the airflow upward, to minimize transfer of alumina from the denuder to the filter of the fluidized bed sampler. The sampler employs Pallflex 2500 QAO quartz fiber filters prefired for several hours at 700°C . The alumina (7 - 12 mesh type F-1, Kaiser Industries, for the denuder, and 40 - 60 mesh Supelco type F-1 for the fluidized bed) was prefired at 400°C to decrease its carbon and water levels. Gaskets for sealing filter holders and the parallel plate denuder were fabricated from Viton and Teflon sheet.
2. A proposed low volatility fine carbon (LVFC) sampler at 20 Lpm employing a cyclone, filter and fluidized bed sampler of the types described above. The gasket employed for the filter holder was fabricated from the spongy rubber material employed in conventional hi-vol samplers.
3. A high volume (hi-vol) sampler equipped with a pyrex cyclone to exclude particles $>3.5 \mu\text{m}$, sampling in tandem with two 8" x 10" quartz filters in the same filter holder at 40 cfm (face velocity 47 cm/sec). The filter medium was as described above. The gasket employed for the filter holder was a spongy rubber not otherwise characterized.
4. A low volume (low-vol) sampler equipped with a stainless steel cyclone (Sierra Model 280-2), through which air was sampled at 20 Lpm to exclude particles $>2.8 \mu\text{m}$. From this fine particle air sample, air was sampled in tandem by two 47 mm quartz filters in the same filter holder at 8 Lpm (face velocity 10 cm/sec). The filter medium was as described above. A neoprene gasket sealed the filter holder.

B. Sunshade

Since solar heating of the sampler inlet might cause enhanced volatilization of carbonaceous material from the sampler, samplers were shielded from the sun with a shade fabricated from wood and corrugated sheet metal mounted in a V-shaped roof above the samplers. The shade was effective except during late afternoon periods because of the low solar angle.

Table 3A. Sampling Strategy for Carbon Intercomparison (10 Days Sampling)

Sampler No.	Sampler	Flow Rate Lpm	Face Velocity cm/sec	Time (hr)	Species Measured
1	Cyclone, parallel plate denuder, Pallflex QAO filter, fluidized bed Total flow thru cyclone 28 Lpm	20	37	12	C_t, C_e, C_o (particle phase)
2	Same as 1 without denuder Total flow thru cyclone 28 Lpm	20	37	13	C_t, C_e, C_o (total)
3	< 3.5 μ m hi-vol, two Pallflex QAO filters	40 (cfm)	50	4 or 8	C_t, C_o, C_e, C_{co_3} (C_t on backup filter)
4	Cyclone of sampler 1, Open face, 47 mm ACHEX filter holder, two Pallflex QAO filters	8.0	9.6	4 or 8	C_t

C. Sampling Location and Schedule

Sampling was done at Citrus College, Glendora, CA during the period Aug. 12 - 20, 1986. Samplers 1 and 2 were operated for 12-hour periods, 0800 - 2000, and 2000 - 0800 hours. Samplers 3 and 4 were operated for 4 or 8 hour periods:

0800 - 1200 Hours PDT
1200 - 1600
1600 - 2000
2000 - 2400
0000 - 0800

The analytical strategy for the atmospheric samples is given in Table 3B.

D. Field Blanks

Immediately following completion of atmospheric sampling, samplers were loaded with five successive sets of sampling media and operated for 30 seconds. Field blanks received the same handling and storage conditions as did the samples.

E. Sample Storage and Handling

Immediately following sampling, filter discs were packaged in Millipore plastic petri dishes stored, in turn, within sealed plastic bags and frozen over dry ice. The 8" x 10" filter samples were packaged in aluminum foil-lined manila folders stored, in turn, within sealed plastic bags and frozen as above. Twenty g alumina portions from samplers 1 and 2 were returned to their original Teflon-lined, screw cap glass test tubes and frozen as above. Following return to the laboratory, the samples were stored at -5°C and only thawed long enough to permit sectioning for the hi-vol filter samples, immediate analysis, for the remaining filter samples, or solvent extraction for the Al_2O_3 .

F. Description of Analyses

1. Total Carbon

Total carbon was determined with a Coulometrics Inc. Model 5010 coulometer and Model 5020 total carbon apparatus. In this technique, the sample is combusted in oxygen with conversion to carbon dioxide aided by $BaCrO_4$. In the coulometer cell, the CO_2 is absorbed by an ethanolamine solution forming a titratable acid. In the automatic coulometric titration, the current generates a base which neutralizes the acid formed by the CO_2 and the result is electronically displayed on the coulometer as μg carbon. Employing a combustion tube temperature of 1200°C, the accuracy of carbon analysis of potassium acid phthalate and graphite was >99% and $97 \pm 2\%$, respectively. To extend heater block lifetime, the combustion tube temperature was reduced to 1100°C midway during the analysis.

**Table 3B. Analyses for Carbon Intercomparisons
(No. of Determinations)**

<u>Sampler</u>	<u>Sample</u>	<u>No. Samples</u>	<u>C_t</u>	<u>C_e (LTM)</u>	<u>CO₃⁻</u>
1	QAO	22	25	25	
2	QAO	20	23	23	
1 and 2	Al ₂ O ₃	42	46		
3	QAO prefilter	50	55	55	10
3	QAO after-filter	50	55		
4	QAO prefilter	50	55		
4	QAO after-filter	50	55		
Totals: 284			314	103	10

of atmospheric samples with no measurable decrease in accuracy with graphite. Under similar conditions, calcium carbonate gave 103 - 104% recovery of carbon, whereas sodium and potassium carbonates yielded recoveries ranging from 84 to 100%. The total carbon analysis is considered to provide the sum of organic, elemental (or "black") carbon and carbonates in atmospheric samples.

2. Carbonate Carbon

Carbonate was determined on a subset of hi-vol filter samples using the Model 5030 carbonate carbon apparatus in which samples are acidified and the evolved CO_2 transferred to the coulometer. With 110 to 210 μg CaCO_3 samples, the recovery of carbon was 84 ± 2.9 (n=4). With Na_2CO_3 , recovery averaged 94.8 ± 1.9 (n=5).

3. Organic Carbon

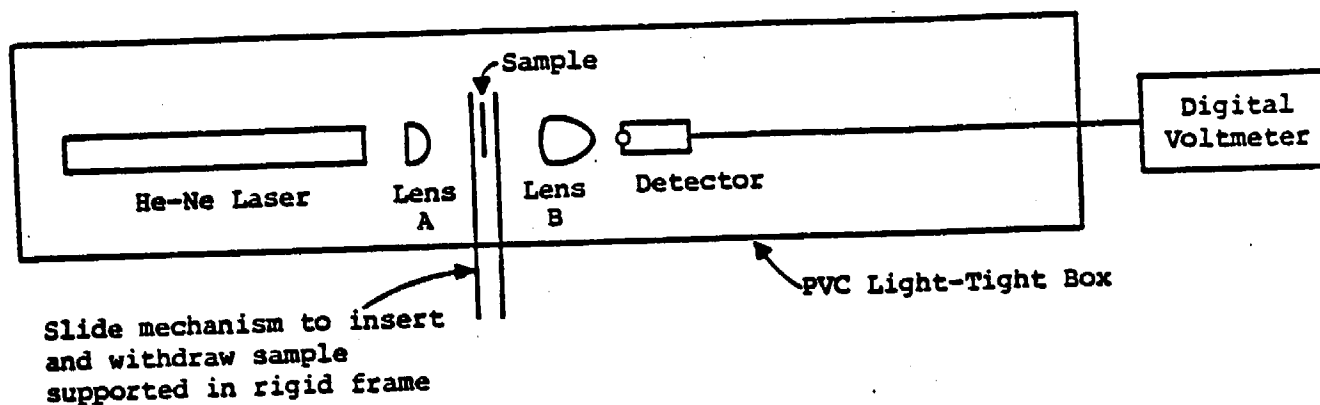
Organic carbon was determined as the difference between total carbon and elemental carbon.

4. Elemental or "Black" Carbon

Elemental carbon was assessed by measuring light absorption with quartz filter samples using a He-Ne laser (632.8 nm) absorption method first described by Rosen et al. (9). This procedure may be considered a version of the integrating plate method (10), with the filter, itself, replacing the integrating plate to provide uniform intensity to all forward-scattered light. A large lens immediately behind the sample is used to focus the light onto the detector. The decrease in light intensity reaching the detector, relative to that for a blank filter, is assumed to be due to light absorption by the particulate matter sample. Furthermore, elemental carbon is assumed to be the only light-absorbing species present. Thus "black carbon" is equated with elemental carbon.

Figure 5 shows the laser transmission method (LTM) apparatus. Our detailed evaluation of this method and comparison to a reflectance and a selective combustion technique has been reported elsewhere (3,4). The earlier results with the LTM showed high correlation against those by the General Motors' combustion technique for elemental carbon ($r=0.97$) but averaged about 15% lower.

In the previously cited studies, the LTM was calibrated against filters loaded with atmospheric and vehicle tunnel particulate matter and analyzed for elemental carbon by a thermal analysis technique, which corrects for decomposition (11). For the present study, the LTM was recalibrated with a number of the same samples. The new calibration is shown in Figure 6.



Laser: 632.8nm, 0.5mW, Spectraphysics Model 155, random polarization.

Lens A: 12.4mm diameter, 14.3mm focal length, plano-convex lens to expand beam to a 1.2cm diameter disc on the filter sample.

Lens B: 60mm diameter, 39mm focal length, aspheric lens, Rolyn optics.

Detector: EG & G Model HUV-1000B silicon photovoltaic detector/operational amplifier combination, positioned at focal point of lens B.

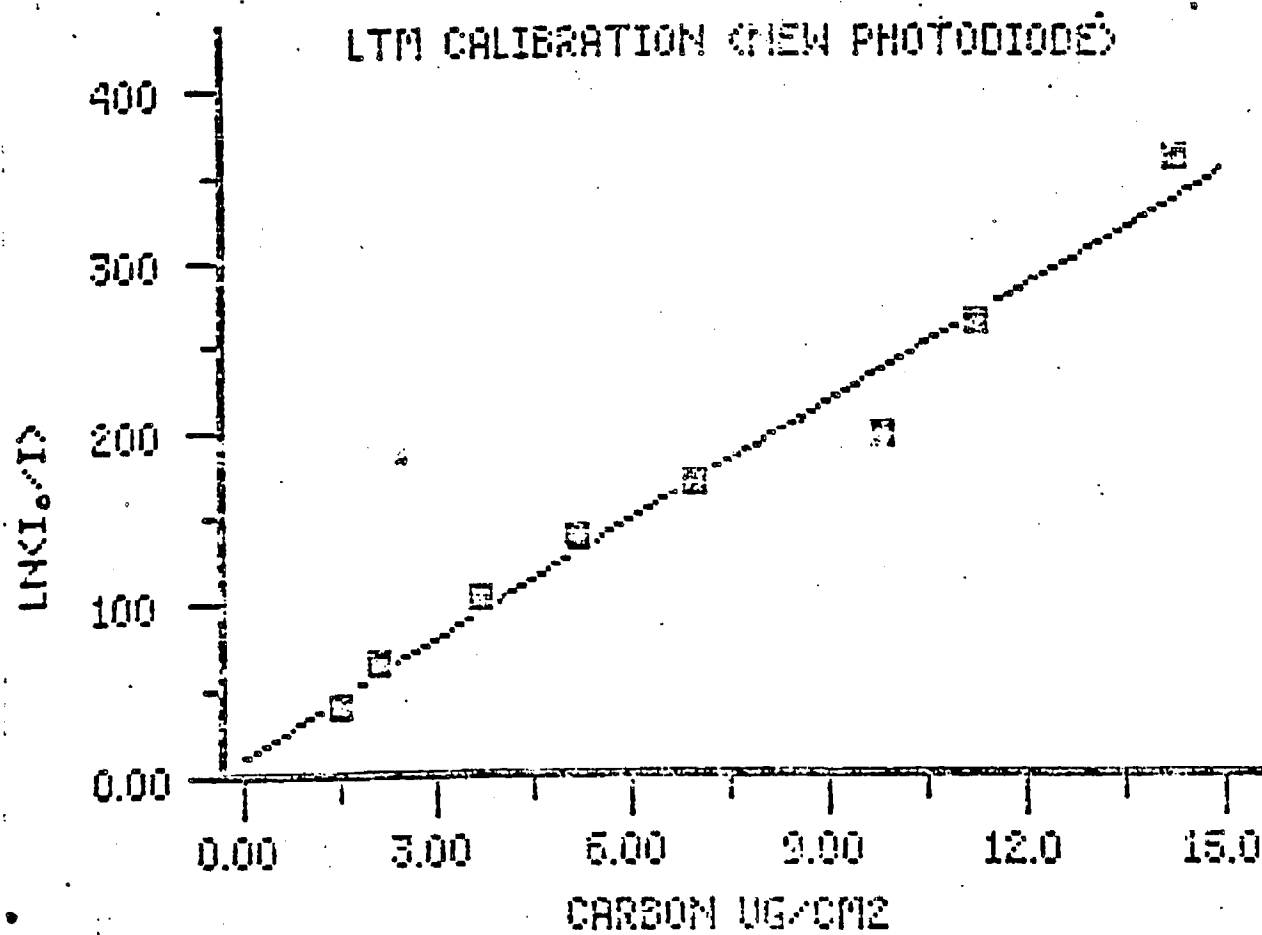
DVM: Fluke Model 8000A digital multimeter.

Base: 1/2" flat steel plate optical bench permitting use of clamps with magnetic bases.

Enclosure: 1/2" PVC sheet.

Figure 5. Schematic Diagram of Laser Transmission Method, Viewed From Above.
(not to scale)

Figure 6.



5. Organic Carbon on Alumina

Recovery of organic compounds retained on the fluidized bed of alumina is done by solvent extraction; 30 ml of methylene chloride (EM SCIENCE, GR Grade), followed, in some cases, by an equal volume of methanol (OMNISOLV glass distilled), is percolated through the 20 g alumina aliquots contained in a 1-cm I.D. chromatography column. Solvent is concentrated to a precisely known volume (ca. 2 ml) in a stream of N₂ while gently heating with an infra-red lamp. Aliquots (0.5 ml) are removed for evaporation in prefired ceramic boats, contained within prefired nickel crucibles (Figure 7), in a stream of particle-free air at room temperature. After evaporation to dryness, the residual organics are measured by total carbon analysis.

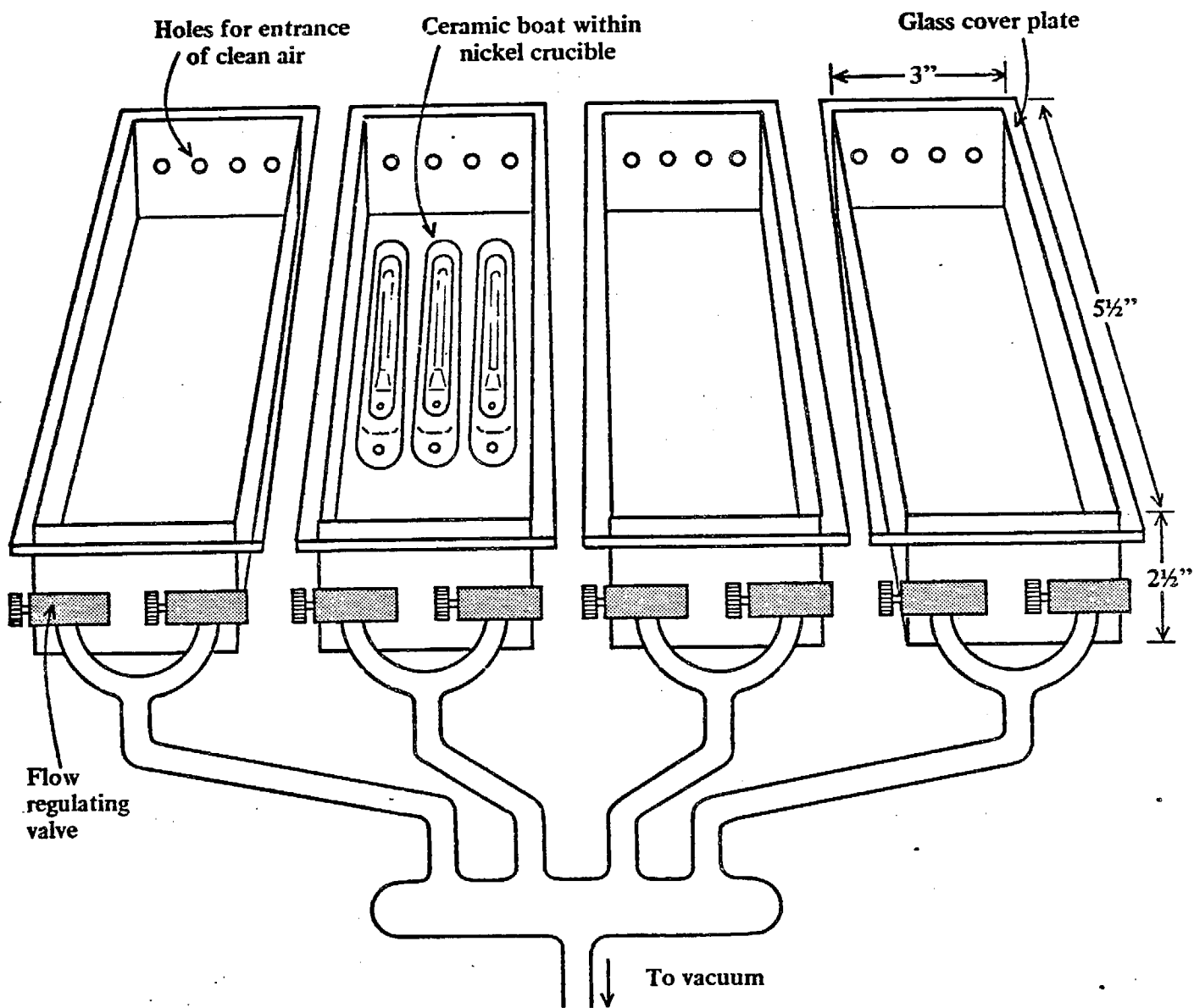


Figure 7. Apparatus for solvent evaporation in clean air at room temperature (shown with boats in one unit).

SOURCE: STATE OF CALIFORNIA
DEPARTMENT OF HEALTH
AIR AND INDUSTRIAL HYGIENE
LABORATORY, BERKELEY

IV. QUALITY ASSURANCE STUDIES

A. Round Robin Samples

Nineteen filter samples were provided by R. Countess, Environmental Monitoring & Services, Inc. (EMSI) representing samples from diesel and gasoline engine exhaust as well as atmospheric samples. The collection medium was Pallflex 2500 QAO in all cases. The samples were analyzed for total carbon and black carbon as described above. The results are listed in Table 4. Two of the samples exceeded the working range for our optical method for black carbon. Accordingly, both C_e and C_o values are unavailable for these samples. Insufficient sample was provided to permit analysis for carbonate carbon. Thus, organic carbon values derived for these samples would include carbonate C_o , if present.

Figure 8 is a scatter diagram of C_e against total carbon for these samples. Excluding samples 3 and 8, C_e correlated well with total carbon: $C_e = 2.70 + 0.138 C_t$, $r = 0.993$ ($n=14$).

The AIHL results in Table 4 were compared to those by the General Motors Research Laboratory. In the GM technique, filter samples are dropped into a furnace at 950°C in a helium carrier gas stream. The evolved pyrolysis products are subsequently converted to CO_2 and analyzed by a non-dispersive infra-red method to yield apparent organic carbon. Oxygen is then introduced into the furnace section containing the sample and the resulting CO_2 is used to measure "apparent elemental carbon". The method is believed to be subject to error from charring during analysis which would yield elevated C_e values. Total carbon is obtained on a second sample section by omitting the initial pyrolysis. For 19 round-robin samples, AIHL results averaged 4.4% higher. The regression equation relating the total carbon data sets is:

$$AIHL = 8.02 + 0.824 (GM) \quad r = 0.994 \quad (n = 19)$$

With organic carbon, for the 12 atmospheric particulate samples, the AIHL results averaged 15% higher:

$$AIHL = -0.391 + 1.15 (GM) \quad r = 0.978 \quad (n = 12)$$

With the auto exhaust particulate and wood smoke samples, the AIHL results averaged 33% higher.

For elemental carbon analyses of atmospheric particulate samples, the AIHL results averaged 17% lower:

$$AIHL = 3.21 + 0.46 (GM) \quad r = 0.938 \quad (n = 12)$$

For the auto exhaust particulate and wood smoke samples, the AIHL results were about half those from GM. Higher GM results with woodsmoke are consistent with the facile carbonization of wood smoke organic components.

Table 4. Carbon Study "Round Robin" Data

Sample No.	Total Carbon Loading $\mu\text{g}/\text{cm}^2$	Error $\mu\text{g}/\text{cm}^2$	Organic Carbon Loading $\mu\text{g}/\text{cm}^2$	Error $\mu\text{g}/\text{cm}^2$	Black Carbon Loading $\mu\text{g}/\text{cm}^2$	Error $\mu\text{g}/\text{cm}^2$ *
Y09-00	1.3	0.2	1.3	0.2	0.0	0.0
Y19-00	11.5	0.2	11.5	0.2	0.0	0.0
Y07-00	40.6	0.5	24.1	0.7	16.5	0.5
Y11-00	129	1.2	N/A	N/A	**	-
Y12-00	13.9	0.3	8.1	0.3	5.1	0.1
Y13-00	101	1.0	84.3	1.1	16.5	0.5
Y15-00	388	3.3	N/A	N/A	**	-
Y18-00	71.5	0.7	63.5	0.7	8.0	0.1
Y10-01	40.1	0.5	31.4	0.5	8.7	0.1
Y17-01	35.6	0.4	28.2	0.4	7.4	0.1
Y02-02	29.8	0.4	23.2	0.4	6.6	0.1
Y03-03	25.6	0.4	19.8	0.4	5.8	0.1
Y01-11	39.5	0.5	31.0	0.5	8.5	0.1
Y20-23	35.9	0.4	28.2	0.4	7.7	0.1
Y06-14	36.2	0.4	28.6	0.5	7.5	0.1
Y05-15	26.2	0.4	20.2	0.4	6.0	0.1
Y14-29	25.9	0.4	20.0	0.4	5.9	0.1
Y08-33	30.1	0.4	23.2	0.4	6.9	0.1
Y04-41	30.1	0.4	23.3	0.4	6.8	0.1
Y16-43	39.7	0.5	31.1	0.5	8.5	0.1

* Precision reflects only repeatability of measurement and does not consider uncertainty of regression equation for calibration.

** Above range of method.

N/A Not available.

TOTAL VS ELEMENTAL CARBON FOR ROBIN

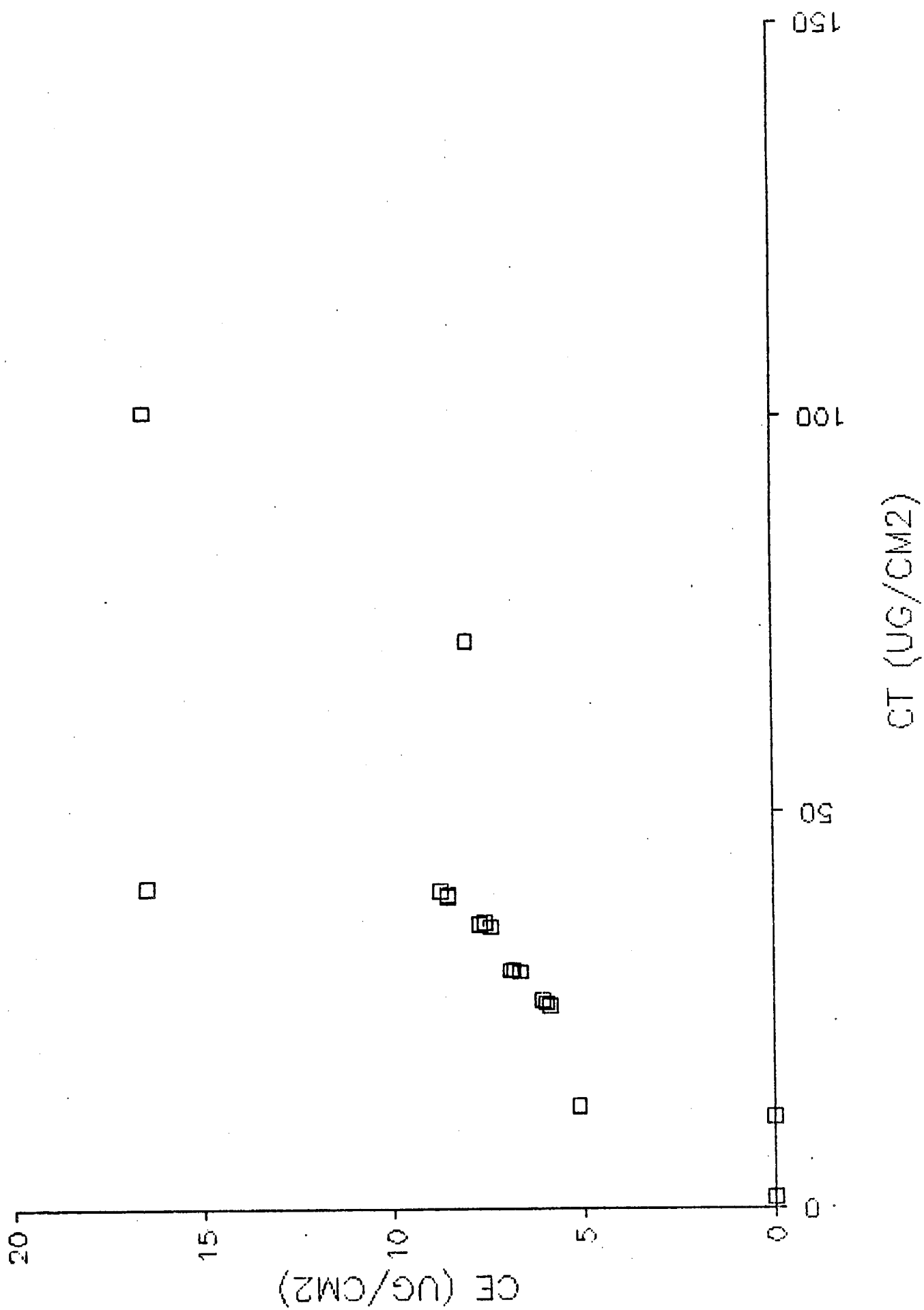


Figure 8.

B. Hi-Vol Filter Samples for Interlaboratory Comparison

In addition to samples supplied by EMSI, ten hi-vol filter samples of atmospheric particulate matter collected at Citrus College were designated for analysis by EMSI as well as by our laboratory. The AIHL results for these samples are given in Table 5 for C_t , C_o , and C_e . For these samples, C_e and C_t showed relatively poor correlation ($r=0.64$) with a pronounced diurnal trend in the proportion of C_e . The proportion of C_e ranged from 18 to 38%, with lowest values between noon and 2000 hours, and highest values overnight. These findings are consistent with an increasing contribution of photochemically generated organic aerosols during afternoon periods.

C. Solvent Removal from Alumina Samples and Effectiveness of an Alumina Parallel Plate Denuder

The major weakness of the strategy for solvent removal is the possibility that residual solvent remains or that some of the atmospheric organic material is lost by volatilization. Rigorous demonstration of the degree of error involved with atmospheric organic materials is probably not feasible. However, QA studies were done to measure the degree of recovery of octadecane from a solution in methylene chloride ($MeCl_2$) and methanol ($MeOH$). In addition, the solvent blank and degree of recovery of atmospheric organic carbon collected on a fluidized bed of alumina was compared using both of the above solvents as well as a 50/50 v/v mixture of the two.

For trials with octadecane (C-18) in $MeCl_2$, 136 μg aliquots in 0.5 ml solvent were delivered into eight ceramic boats. Evaporations of $MeCl_2$ were done for 15, 30 and 45 min. in air and for 15 min in air followed by 15 min. in vacuum (estimated pressure <5 torr) all at room temperature. With $MeOH$ solutions, conditions were the same, except that the 15 to 45 minutes evaporation times followed an initial 40 min. evaporation in air needed to evaporate all visible solvent. The results are given in Table 6. Recovery of C-18 from $MeCl_2$ extracts remained unchanged over the interval 15 to 30 min evaporation time in air. Use of vacuum decreased recovery by about 20%.

For trials with $MeOH$ solutions, 27 μg aliquots of C-18 in 0.5 ml solvent were used, other conditions being as described previously. The results given in Table 6, again, show no significant loss at atmospheric pressure. However, in vacuum, loss of as much as 60% of the C-18 was observed. As with $MeCl_2$, these results demonstrate that quantitative removal of solvent by room temperature evaporation at atmospheric pressure is readily accomplished.

The blank value for solvent extraction with $MeCl_2$ was assessed, comparing total carbon residues from the standard 20 g Al_2O_3 samples after 15 minute evaporations in air to C_t values with an additional 15 and 30 min. in vacuum. Blank values determined were 6.2, 3.2 and 8.7 μg , respectively.

Table 5

FIELD SAMPLES ALSO ANALYZED BY EMSI

UG/CM2, UNCORRECTED FOR BLANK			START	STOP	ORGANIC	CARBON	BLACK CARBON	TOTAL CARBON				
NO.GROUP	SAMPLER	SAMPLE	START	TIME	TIME	LOADING	ERROR	LOADING	ERROR	LOADING	ERROR	
		NUMBER	DATE	(PDT)	(PDT)	UG/CM2	UG/CM2	UG/CM2	UG/CM2	UG/CM2	UG/CM2	
1	APPEL	#3	41AT3P'	8-14	0806	1150	12.5	.5	4.4	.1	17.0	.5
2	APPEL	#3	42AT3P'	8-14	1153	1557	15.6	.6	3.9	.1	19.5	.6
3	APPEL	#3	43AT3P'	8-14	1559	1959	16.4	.6	3.7	.1	20.1	.6
4	APPEL	#3	44AT3P'	8-14	2002	2358	8.4	.3	2.7	.1	11.1	.3
5	APPEL	#3	45AT3P'	8-14	2359	0759	8.5	.4	5.2	.1	13.7	.4
6	APPEL	#3	91AT3P'	8-19	0756	1201	13.2	.5	3.3	.1	16.5	.5
7	APPEL	#3	92AT3P'	8-19	1204	1600	14.3	.5	3.1	.1	17.4	.5
8	APPEL	#3	93AT3P'	8-19	1602	2000	7.8	.3	1.7	.1	9.5	.3
9	APPEL	#3	94AT3P'	8-19	2004	2359	8.0	.3	2.1	.1	10.0	.3
10	APPEL	#3	95AT3P'	8-19	2401	0800	15.3	.6	4.5	.1	19.8	.6

UG/CM2, CORRECTED FOR BLANK			START	STOP	ORGANIC	CARBON	BLACK CARBON	TOTAL CARBON				
NO.GROUP	SAMPLER	SAMPLE	START	TIME	TIME	LOADING	ERROR	LOADING	ERROR	LOADING	ERROR	
		NUMBER	DATE	(PDT)	(PDT)	UG/CM2	UG/CM2	UG/CM2	UG/CM2	UG/CM2	UG/CM2	
1	APPEL	#3	41AT3P'	8-14	0806	1150	12.0	.5	4.4	.1	16.4	.5
2	APPEL	#3	42AT3P'	8-14	1153	1557	15.1	.6	3.9	.1	19.0	.6
3	APPEL	#3	43AT3P'	8-14	1559	1959	15.9	.6	3.7	.1	19.5	.6
4	APPEL	#3	44AT3P'	8-14	2002	2358	7.9	.3	2.7	.1	10.6	.3
5	APPEL	#3	45AT3P'	8-14	2359	0759	8.0	.4	5.2	.1	13.2	.4
6	APPEL	#3	91AT3P'	8-19	0756	1201	12.7	.5	3.3	.1	15.9	.5
7	APPEL	#3	92AT3P'	8-19	1204	1600	13.8	.5	3.1	.1	16.9	.5
8	APPEL	#3	93AT3P'	8-19	1602	2000	7.3	.3	1.7	.1	9.0	.3
9	APPEL	#3	94AT3P	8-19	2004	2359	7.4	.3	2.1	.1	9.5	.3
10	APPEL	#3	95AT3P'	8-19	2401	0800	14.8	.6	4.5	.1	19.3	.6

UG/M3, CORRECTED FOR BLANK			START	STOP	ORGANIC	CARBON	BLACK CARBON	TOTAL CARBON				
NO.GROUP	SAMPLER	SAMPLE	START	TIME	TIME	LOADING	ERROR	LOADING	ERROR	LOADING	ERROR	
		NUMBER	DATE	(PDT)	(PDT)	UG/m3	UG/m3	UG/m3	UG/m3	UG/m3	UG/m3	
1	APPEL	#3	41AT3P'	8-14	0806	1150	18.9	1.6	7.0	.4	25.9	1.5
2	APPEL	#3	42AT3P'	8-14	1153	1557	21.9	1.6	5.7	.3	27.6	1.6
3	APPEL	#3	43AT3P'	8-14	1559	1959	23.0	1.7	5.3	.3	28.4	1.7
4	APPEL	#3	44AT3P'	8-14	2002	2358	11.8	1.0	4.0	.2	15.8	.9
5	APPEL	#3	45AT3P'	8-14	2359	0759	5.8	.6	3.8	.2	9.5	.6
6	APPEL	#3	91AT3P'	8-19	0756	1201	18.3	1.4	4.7	.3	23.1	1.3
7	APPEL	#3	92AT3P'	8-19	1204	1600	20.6	1.5	4.6	.3	25.2	1.5
8	APPEL	#3	93AT3P'	8-19	1602	2000	10.5	.8	2.4	.2	13.0	.8
9	APPEL	#3	94AT3P	8-19	2004	2359	11.2	.9	3.1	.2	14.3	.8
10	APPEL	#3	95AT3P'	8-19	2401	0800	10.9	.8	3.3	.2	14.2	.8

Table 6. Recovery of Octadecane from Solvents After Evaporation^a

Solvent	Evaporation Time (Minutes)							
	15		30		45		15 + 15 vacuum	
	<u>μg C</u>	<u>%</u>	<u>μg C</u>	<u>%</u>	<u>μg C</u>	<u>%</u>	<u>μg C</u>	<u>%</u>
MeCl ₂	122 ± 4.2	106	125 ± 0	109	121 ± 0.2	105	101 ± 2.8	87.8
MeOH	26.4 ± 1.3	115	26.2 ± 1.1	114	25 ± 5.7	109	15 ± 5.4	65

- a. Results are means ± one sigma for evaporation of two aliquots to dryness.
- b. Evaporation times for MeOH measured following an initial 40 min. required to evaporate all visible solvent. Thus total evaporation times are 55, 70 and 85 minutes in air or 55 min. in air plus 15 min. in vacuum.

For recovery studies with atmospheric carbonaceous material, laboratory room air was sampled for 28 hours by a fine particulate carbon (FPC) sampler in parallel with a low volatility fine carbon (LVFC) sampler. The alumina in both samplers was divided in half, one half being extracted with dichloromethane (MeCl_2) followed by MeOH, and the other with 50/50 (by volume) MeCl_2 -MeOH mixed solvent. Carbon from the filters in this case was not determined. Recoveries of the atmospheric carbon from the Al_2O_3 for the LVFC and FPC samplers are shown in Table 7 and 8, respectively. The reproducibility of MeCl_2 recovery with 15 min air evaporation of 0.5 ml aliquots was good. This and slightly lower values for 45 min air evaporation suggested that the residual solvent was totally removed within 15 min air evaporation. The recovery of carbon following vacuum treatment was usually lower than the corresponding value under air evaporation for all three solvents. Recovery of atmospheric carbon with the 50/50 mixed solvent was very poor, compared to that by successive extractions in the pure solvents. The recovery of carbon from subsequent MeOH extraction for the LVFC sampler was about 37% of that from MeCl_2 , confirming that there is a significant amount of polar organics in the air sample, which would require elution with a more polar solvent.

The recovered carbon from the MeCl_2 extract of the FPC sampler was 23% lower than the corresponding value for LVFC sampler, whereas the recovered carbon from the MeOH extract for the FPC was below detection compared to 190 μg for the corresponding value for the LVFC. It appears that the denuder is capable of retaining polar organic materials present as gaseous pollutants, but is less efficient in removing low polarity organic compounds capturable on the fluidized bed.

Regarding extraction methodology, these results indicate (1) the importance of using the less polar solvent for sample elution, (2) that 15 minutes in a flowing stream of air is sufficient to remove MeCl_2 from 0.5 ml extracts of atmospheric organic materials, and (3) that vacuum treatment should be avoided to minimize sample loss.

D. QA Experiment at Citrus College with the Proposed FPC Sampler

The denuder of the FPC sampler is intended to remove with all vapor-phase carbonaceous materials which, otherwise, would be retained by the filter and/or the fluidized bed. Accordingly, if an efficient particle filter precedes the FPC sampler, and if volatilized carbonaceous material does not re-condense downstream of this prefilter, then only vapor-phase materials enter the unit and no carbon should be measured on the FPC sampler.

Two 12-hour trials were made in which the FPC and LVFC samplers operated in parallel, both being preceded by separate, 102 mm prefilters. In the first experiment, a Teflon prefilter was employed, and in the second, a Pallflex QAO filter.

Table 7. Recovery of Atmospheric Carbon from Al_2O_3 by Solvent Extraction for the LVPC Sampler^a

Solvent	Volume (mL)	Evaporation Conditions ^b					
		15 min. in air		45 min. in air		15 min. in vacuum	
		μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$
MeCl_2	30	526 ± 69	15.2 ± 2.0	-	-	-	-
MeOH	20			190 ± 31	5.7 ± 0.9	135	4.0
1:1 v/v MeCl_2 - MeOH	30			96.3 ± 7.6	2.9 ± 0.2	82.1	2.4

a. Results uncorrected for blanks.

b. With MeCl_2 , follows 15 min. evaporation in air. With MeOH, follows 45 min. evaporation in air, and with mixed solvent, follows 30 min. evaporation in air.

Table 8. Recovery of Atmospheric Carbon from Alumina by Solvent Extraction for the FPC Sampler^a

Solvent	Volume (ml)	Evaporation Conditions					
		15 min. in air		n min. in air ^b		15 min. in vacuum ^c	
		μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$
MeCl ₂	30	405 ± 6.5	12.0 ± 0.2	-	-	352	9.3
MeOH	20			-3.9 ± 7.7	0	16.4	0.5
1:1 v/v MeCl ₂ - MeOH	30			93.2 ± 13.5	2.8 ± 0.4	14.4	0.4

a. Results uncorrected for blanks.

b. n = 45 with MeOH and 30 with the mixed solvent.

c. With MeCl₂, follows 15 min. evaporation in air. With MeOH, follows 45 min. evaporation in air, and with the mixed solvent, follows 30 min. evaporation in air.

Inspection of the quartz filter in the FPC sampler from the first trial revealed a grey deposit suggesting atmospheric particle penetration, probably due to an inadequate seal on the 102 mm Teflon prefilter. Accordingly, samples from this trial were discarded. With the second trial, however, no such penetration was evident. The results are summarized in Table 9. Blank corrections employed were field blank values obtained with filters loaded for 30 seconds in each sampler (see below). Without the denuder, 9 $\mu\text{g}/\text{m}^3$ of carbon was recovered from the sampling media, 31% of which was retained on the quartz filter just ahead of the fluidized bed. Of the remaining carbon (recovered from the alumina) nearly three-fourths was sufficiently non-polar to be eluted with MeCl_2 . With the denuder present, the total recovered carbon was not zero as desired, but was reduced by 56% from that without the denuder. Most of the reduction is evident in the carbon recovered from the alumina; carbon eluted with MeCl_2 was reduced by 70% while the low level of polar carbon was reduced by about 90%. By contrast, carbon recovered from the quartz filter was only 12% lower.

Possible explanations of these results are (1) that the alumina denuder was relatively ineffectual for vapor phase carbonaceous material able to be retained on the quartz filter, (2) that volatilization of carbonaceous material from the prefilter during the late afternoon period followed by re-condensation distorted the results, (3) that some of the alumina (probably containing about 1000 ppm(w) carbon from CO_2 sorption) was being transferred from the denuder to the filter following it. Such alumina would contain adsorbed CO_2 as well as organic materials, or (4) that the samplers contained other sources of carbon transferable to the filter.

Regarding retention on quartz filters of carbonaceous materials not readily removed with the Al_2O_3 denuder, studies at AIHL sponsored by the U.S. EPA have assessed the retention of CO_2 , formic and acetic acids, and formaldehyde on filters of varying alkalinity. Of these, only formic acid and CO_2 showed significant retention. Formic acid retention paralleled filter alkalinity, and was negligible with quartz filters. With CO_2 in humidified air, alkaline filters showed no retention, but such retention was measurable, by total carbon analysis, with non-alkaline filters, including pre-fired Pallflex Quartz 2500 QAO. With an atmosphere containing 50%v CO_2 at 70-75% R.H. and room temperature, CO_2 retention appeared to be 22 $\mu\text{g}/47$ mm disc, or 1.3 $\mu\text{g}/\text{cm}^2$ as carbon. Since total carbon analyses were used, some of the observed carbon may be due to retention of organic materials present in the purified ambient air. For the filters used in samplers 1 and 2, the observed carbon corresponds to 21 μg carbon as an upper limit to the atmospheric CO_2 contribution expected in the present study. This compares to levels of 35 to 40 μgC (Table 9) in the Citrus College trial.

Regarding transfer of carbon from components of the system, the 4-inch diameter prefilter ahead of the proposed FPC sampler in this QA experiment employed neoprene O-rings for filter sealing. Laboratory experiments were conducted to assess the possible contribu-

Table 9. Atmospheric Sampling at Citrus College with the FPC and LVFC Samplers Each Preceded by Single Quartz Fiber Filters^a

Sampler No.	Recovery of Total Carbon (μg)							
	Filter		Al_2O_3 with MeCl_2		Al_2O_3 with MeOH		Σ Carbon	
	μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$	μg	$\mu\text{g}/\text{m}^3$
1 (with denuder)	34.9	2.4	19.9	1.4	2.3	0.16	57.1	4.0
2 (no denuder)	39.9	2.8	64.4	4.5	24.4	1.7	128.7	9.0

a. Blank corrections are those from Table 11.

tion of neoprene gaskets to quartz filter-collected carbon. Initial findings with this gasket indicated insignificant levels of carbon from this source.

E. Precision, Field Blanks, and Limits of Detection for Total Carbon

Measurement of analytical precision for total carbon determinations was limited to 8" x 10" filter samples (sampler 3). With these samples, the aliquot analyzed, 3.2 cm in diameter, permitted multiple determinations. With samplers 1, 2 and 4, filter diameter was 4.7 cm or less. Use of an aliquot sufficiently small to allow multiple analyses would, itself, diminish precision. Accordingly, the complete filters were analyzed.

Table 10 lists results for two determinations on each of 10 samples, chosen to represent the complete range of loadings experienced with the hi-vol front filters. Analyses shown were by different analysts separated in time by about two months. The coefficients of variation ranged from 0.2 to 3.8%, with a median C.V. of 1.7%. Additionally, five determinations of a sample with about 155 μg loading, performed on the same day, gave a C.V. of 1.8%.

Field blank total carbon values are listed in Table 11. In general, five field blanks were analyzed with each sample type. With sampler 4, field blanks for both prefilters and after-filters were analyzed, confirming the expectation of no significant difference. Sampler 3 prefilter field blanks were analyzed twice, with good agreement between trials.

Field blank results for sampler 1 and 2 filters, although still quite low, were more than twice the values for samplers 3 and 4, even though the same filter medium and similar filter pretreatment were employed. Sampler 1 and 2 filters are in direct contact with large Viton gaskets, which raised concern about a time-dependent transfer of carbon to the filter. However, laboratory simulation, with filter-gasket contact for 2 minutes or 4 hours showed values unchanged from those given in the table for samplers 1 and 2. Sample contamination from storage in Millipore plastic petri dishes was similarly ruled out. The cause of the higher blank values for samplers 1 and 2 remains unknown.

The sorption of CO_2 on quartz filters of the type used here suggests that the strategy for field blank measurement cited above, may be inappropriate for correcting atmospheric results. If sorption of CO_2 is the predominant source of increase in the filter blank, then blank corrections based on sampling purified air containing CO_2 might be the preferred strategy. The precision for very lightly loaded filter samples may be inferred from these field blank results which showed standard deviations ranging from 0.04 to 0.36 $\mu\text{g}/\text{cm}^2$ (median 0.18 $\mu\text{g}/\text{cm}^2$). Limits of detection were calculated based on twice the standard deviations for each field blank and the typical air volume sampled. Such limits of detection, expressed in $\mu\text{g}/\text{m}^3$, are also listed in Table 11.

Table 10. Precision of Total Carbon Determinations on Sampler 3 (Hi-Vol) Quartz Filter Samples

<u>Sampling Period</u>	<u>First Measurement Date</u>	<u>$\mu\text{g/sample}^a$</u>	<u>Second Measurement Date</u>	<u>$\mu\text{g/sample}^a$</u>	<u>C.V. (%)</u>
54	09/11/86	65.9	11/04/86	66.9	1.1
74	08/17/86	71.0	11/04/86	70.1	0.9
84	09/11/86	89.3	11/04/86	85.3	3.2
73	08/28/86	111.7	11/04/86	109.3	1.5
85	09/04/86	118.3	11/04/86	119.3	0.6
51	09/11/86	125.7	11/04/86	125.3	0.2
71	08/28/86	140.2	11/04/86	132.8	3.8
65	09/05/86	163.7	11/04/86	161.0	1.9
52	09/11/86	182.8	11/04/86	188.3	2.1
105	09/03/86	189.8	11/04/86	185.0	1.8
					<hr/> Median C.V. = 1.7%

a. Filter punch diameter 3.18 cm.

Table 11. Summary of Field Blank Results for Total Carbon^d

Sampler No.	Media Type	Aliquot Size	Total C		Limits of Detection ($\mu\text{g}/\text{m}^3$)
			μg	$\mu\text{g}/\text{cm}^2$	
1	Pallflex QAO filter	16.26 cm^2	17.6 \pm 2.9	1.08 \pm 0.18	0.4 ^a
1 and 2	40/60 Mesh Al_2O_3	20 g	1.52 \pm 0.76 (MeCl_2) 0.68 \pm 0.096 (MeOH)		0.10 ^a
2	Pallflex QAO filter	16.26 cm^2	18.0 \pm 5.8	1.11 \pm 0.36	0.7 ^a
3 (prefilter)	Pallflex QAO filter	7.88 cm^2	3.9 \pm 1.8	0.50 \pm 0.23	0.7 ^b
3 (after-filter)	Pallflex QAO filter	7.88 cm^2	4.2 \pm 1.7	0.53 \pm 0.22	0.6 ^b
4 (prefilter)	Pallflex QAO filter	17.35 cm^2	8.4 \pm 2.8	0.48 \pm 0.16	2.9 ^c
4 (after-filter)	Pallflex QAO filter	17.35 cm^2	7.7 \pm 0.7	0.44 \pm 0.04	0.7 ^c

a. For 12-hour samples at 20 Lpm

b. For 4-hour samples at 1.1 m^3/min

c. For 4-hour samples at 8 Lpm

d. n = 5

Field blank values for elemental carbon on filters were not measurably different from zero. A lower limit for reliable quantitation of $1 \mu\text{g}/\text{cm}^2$ for C_e was estimated, based on the lowest standard used in the calibration of the laser transmission method. The corresponding limits, in $\mu\text{g}/\text{m}^3$, are given in Table 12. As a result of the low flow rate employed, the lower limit for sampler 4 was relatively high. Only five atmospheric samples from sampler 4 exceeded these limits for C_e .

F. Carbonate Analysis of Atmospheric Particulate Matter

1. Introduction

The determination of organic carbon as the difference between C_t and C_e is subject to error if carbonate C is present:

$$C_o = C_t - C_e - C_{\text{CO}_3}$$

Previous studies have shown that, with urban air samples, carbonate was a negligible contributor to C_t (12). To insure that this was likely to be the case in the present study, selected hi-vol (sampler 3) prefilter samples were analyzed for carbonate. Samples analyzed ranged in C_o from 8 to $26 \mu\text{g}/\text{m}^3$ (the highest observed value). In addition to prefilters, after-filters, which showed total carbon values from 5 to $6.5 \mu\text{g}/\text{m}^3$, were analyzed for carbonate seeking evidence of the retention of atmospheric CO_2 on quartz filters.

2. Results

Table 13 summarizes results for field blanks, prefilters and after-filters. Although the precision of field blank determinations was excellent, most of the samples showed carbonate carbon values below those of the field blanks, resulting in small negative corrected sample results. We conclude that carbonate on both prefilters and after-filters was $<1 \mu\text{g C/sample}$, which, for 4-hour samples, corresponds to an upper limit of $0.24 \mu\text{g}/\text{m}^3$ as C. Accordingly, it is unlikely that carbonate or atmospheric CO_2 contributed significantly to the calculated C_o with any field filter sample.

Table 12. Estimation of Lower Limits for Reliable Quantitation of Elemental Carbon on Filters by the Laser Transmission Method

<u>Sampler</u>	<u>Lower Limit</u>	
	<u>$\mu\text{g}/\text{cm}^2$</u>	<u>$\mu\text{g}/\text{m}^3$</u>
1	1.0	0.7 ^a
2	1.0	0.7 ^a
3	1.0	1.5 ^b
4	1.0	7.2 ^{c,d}

- a. For 12-hour samples at 20 Lpm
- b. For 4-hour samples at 1.1 m³/min
- c. For 4-hour samples at 8 Lpm
- d. 3.6 $\mu\text{g}/\text{m}^3$ for 8-hour samples.

Table 13. Carbonate Analysis of Filter Samples

<u>Sample I.D.</u>	<u>Carbonate as C</u> <u>µg/sample^a</u>
21 AT3P	0.7
22 AT3P	-0.5
23 AT3P	-0.1
24 AT3P	-0.2
25 AT3P	-1.0
21 AT3A	0.2
22 AT3A	-0.1
52 AT3A	-0.1

a. Sample size 6.53 cm². Results following subtraction of mean field blank, 2.97 ± 0.06 µg C per 6.53 cm² (n=3).

V. SUMMARY OF ATMOSPHERIC RESULTS

Table 14 is a chronological listing of all results and associated standard deviations for atmospheric samples. To assist in comparison of results, Table 15 includes the same results sorted both chronologically and by sampler number.

Table 14

CARBON STUDY FIELD SAMPLES												
A B GROUP	SAMPLE SAMPLE	START No.	START DATE	TIME (PDT)	STOP TIME (PDT)	ORG. C LOADING UgC/m3	ORG. C ERROR UgC/m3	VOLUME m3	ELEM C LOADING UgC/m3	ELEM C ERROR UgC/m3	TOTAL C LOADING UgC/m3	TOT C. ERROR UgC/m3
APPEL	3	21AT3P	8/12	0800	1157	18.79	2.08	266.83	9.84	1.43	28.63	1.51
APPEL	3	21AT3A	8/12	0800	1157	5.04	.37	266.83	0	0	5.04	.27
APPEL	4	21AT4P	8/12	0800	1157	36.64	2.13	1.97	7.57	1.33	44.21	1.66
APPEL	4	21AT4A	8/12	0800	1157	23.96	1.27	1.97	0	0	23.96	1.05
APPEL	3	22AT3P	8/12	1218	1553	22.88	2.09	242.06	5.91	1.44	28.79	1.52
APPEL	3	22AT3A	8/12	1218	1553	5.51	.4	242.06	0	0	5.51	.29
APPEL	4	22AT4P	8/12	1212	1555	45.34	2.2	1.78	<7.78	0	45.34	1.73
APPEL	4	22AT4A	8/12	1212	1555	15.67	.97	1.78	0	0	15.67	.85
APPEL	3	23AT3P	8/12	1554	1953	12.94	1.2	281.03	3.47	.82	16.41	.87
APPEL	3	23AT3A	8/12	1554	1953	3.56	.26	281.03	0	0	3.56	.19
APPEL	4	23AT4P	8/12	1605	1956	26.01	1.37	1.83	<7.57	0	26.01	1.13
APPEL	4	23AT4A	8/12	1605	1956	7.7	.68	1.83	0	0	7.70	.64
APPEL	3	24AT3P	8/12	1955	2355	11.08	1.15	270.21	4.76	.79	15.84	.84
APPEL	3	24AT3A	8/12	1955	2355	2.55	.18	270.21	0	0	2.55	.13
APPEL	4	24AT4P	8/12	1957	2358	28.65	1.47	1.93	<7.18	0	28.65	1.19
APPEL	4	24AT4A	8/12	1957	2358	9.22	.71	1.93	0	0	9.22	.65
APPEL	3	25AT3P	8/12	2357	0810	7.49	.94	542.77	5.22	.65	12.91	.68
APPEL	3	25AT3A	8/12	2357	0810	2.35	.17	542.77	0	0	2.35	.12
APPEL	4	25AT4P	8/12	2400	0808	13.4	.91	3.9	4.96	.55	18.36	.72
APPEL	4	25AT4A	8/12	2400	0808	3.69	.32	3.9	0	0	3.69	.3
APPEL	1	26AD1F	8/12	0800	1958	16.52	1.05	14.68	5.59	.70	22.11	.74
APPEL	1	26AD1S	8/12	0800	1958	11.15	.42	14.68	0	0	11.15	.42
APPEL	2	26AF2F	8/12	0800	1958	16.89	1.01	14.49	5.39	.67	22.28	.75
APPEL	2	26AF2S	8/12	0800	1958	11.43	.43	14.49	0	0	11.43	.43
APPEL	1	27AD1F	8/12	2024	0751	10.53	.73	13.74	5.60	.48	16.13	.55
APPEL	1	27AD1S	8/12	2024	0751	16.59	.6	13.74	0	0	16.59	.6
APPEL	2	27AF2F	8/12	2024	0751	9.01	.62	13.74	4.57	.41	13.58	.47
APPEL	2	27AF2S	8/12	2024	0751	3.25	.2	13.74	0	0	3.25	.2
APPEL	3	31AT3P	8/13	0815	1155	16.45	1.83	249.19	8.65	1.26	25.10	1.33
APPEL	3	31AT3A	8/13	0815	1155	4.1	.3	249.19	0	0	4.10	.22
APPEL	4	31AT4P	8/13	0809	1159	40.27	1.97	1.88	<7.37	0	40.27	1.56
APPEL	4	31AT4A	8/13	0809	1159	9.79	.74	1.88	0	0	9.79	.68
APPEL	3	32AT3P	8/13	1157	1158	17.99	1.75	271.34	6.04	1.20	24.03	1.27
APPEL	3	32AT3A	8/13	1157	1158	3.74	.28	271.34	0	0	3.74	.2
APPEL	4	32AT4P	8/13	1200	1600	37.14	1.83	1.96	<7.07	0	37.14	1.45
APPEL	4	32AT4A	8/13	1200	1600	12.91	.84	1.96	0	0	12.91	.74
APPEL	3	33AT3P	8/13	1600	2000	19.01	1.72	273.2	4.63	1.18	23.64	1.25
APPEL	3	33AT3A	8/13	1600	2000	3.75	.28	273.2	0	0	3.75	.2
APPEL	4	33AT4P	8/13	1601	2001	35.21	1.75	1.92	<7.21	0	35.21	1.39
APPEL	4	33AT4A	8/13	1601	2001	9.69	.73	1.92	0	0	9.69	.67
APPEL	3	34AT3P	8/13	2001	2401	10.77	1.09	273.2	4.23	.75	15.00	.79
APPEL	3	34AT3A	8/13	2001	2401	2.48	.18	273.2	0	0	2.48	.13
APPEL	4	34AT4P	8/13	2002	2404	21.09	1.16	1.92	<7.21	0	21.09	.97
APPEL	4	34AT4A	8/13	2002	2404	7.5	.66	1.92	0	0	7.50	.62
APPEL	3	35AT3P	8/13	2403	0804	7.71	.88	544.82	4.40	.61	12.11	.64
APPEL	3	35AT3A	8/13	2403	0804	1.74	.13	544.82	0	0	1.74	.09
APPEL	4	35AT4P	8/13	2406	0801	14.67	.91	3.8	3.67	.55	18.34	.72
APPEL	4	35AT4A	8/13	2406	0801	4.58	.36	3.8	0	0	4.58	.33
APPEL	1	36AD1F	8/13	0803	2003	14.94	.93	14.9	5.63	.62	20.57	.69
APPEL	1	36AD1S	8/13	0803	2003	8.08	.33	14.9	0	0	8.08	.33
APPEL	2	36AF2F	8/13	0803	2003	15.56	.96	14.4	5.79	.64	21.35	.72
APPEL	2	36AF2S	8/13	0803	2003	5.18	.24	14.4	0	0	5.18	.24
APPEL	1	37AD1F	8/13	2030	0745	9.13	.61	13.44	4.23	.40	13.36	.46
APPEL	1	37AD1S	8/13	2030	0745	3.12	.19	13.44	0	0	3.12	.19
APPEL	2	37AF2F	8/13	2028	0745	10.37	.67	13.48	4.33	.44	14.70	.51
APPEL	2	37AF2S	8/13	2028	0745	2.46	.18	13.48	0	0	2.46	.18
APPEL	3	41AT3P	8/14	0806	1150	18.47	1.85	252.2	6.96	1.27	25.43	1.34
APPEL	3	41AT3A	8/14	0806	1150	6.2	.45	252.2	0	0	6.20	.33

APPEL	4	41AT4A	8/14	0802	1154	9.89	.74	1.9	0	0	9.89	.68
APPEL	3	42AT3P	8/14	1153	1157	21.54	1.98	273.19	5.70	1.36	27.24	1.44
APPEL	3	42AT3A	8/14	1153	1157	5.22	.38	279.19	0	0	5.22	.28
APPEL	4	42AT4P	8/14	1155	1558	39.2	1.92	1.99	<6.96	0	39.20	1.51
APPEL	4	42AT4A	8/14	1155	1558	13.57	.85	1.99	0	0	13.57	.75
APPEL	3	43AT3P	8/14	1559	1959	22.51	2.02	273.2	5.32	1.39	27.83	1.47
APPEL	3	43AT3A	8/14	1559	1959	5.2	.38	273.2	0	0	5.20	.28
APPEL	4	43AT4P	8/14	1558	1958	41.21	2.01	1.9	<7.29	0	41.21	1.58
APPEL	4	43AT4A	8/14	1558	1958	6.63	.63	1.9	0	0	6.63	.6
APPEL	3	44AT3P	8/14	2002	2358	11.26	1.11	267.31	4.01	.76	15.27	.81
APPEL	3	44AT3A	8/14	2002	2358	2.22	.16	267.31	0	0	2.22	.12
APPEL	4	44AT4P	8/14	2000	2358	28.74	1.48	1.9	<7.29	0	28.74	1.2
APPEL	4	44AT4A	8/14	2000	2358	4.74	.58	1.9	0	0	4.74	.56
APPEL	3	45AT3P	8/14	2359	0759	5.66	.69	549.39	3.76	.47	9.42	.5
APPEL	3	45AT3A	8/14	2359	0759	1.55	.11	549.39	0	0	1.55	.08
APPEL	4	45AT4P	8/14	2358	0758	14.9	.76	3.84	<3.61	0	14.90	.61
APPEL	4	45AT4A	8/14	2358	0758	15.57	.79	3.84	0	0	15.57	.63
APPEL	1	46AD1F	8/14	0800	2000	18.2	1.06	14.4	5.35	.71	23.55	.79
APPEL	1	46AD1S	8/14	0800	2000	5.51	.25	14.4	0	0	5.51	.25
APPEL	2	46AF2F	8/14	0800	2000	19.12	1.1	14.4	5.54	.74	24.66	.82
APPEL	2	46AF2S	8/14	0800	2000	7.08	.3	14.4	0	0	7.08	.3
APPEL	1	47AD1F	8/14	2020	0740	7.52	.52	13.72	3.73	.34	11.25	.39
APPEL	1	47AD1S	8/14	2020	0740	8.18	.34	13.72	0	0	8.18	.34
APPEL	2	47AF2F	8/14	2020	0740	7.53	.52	13.6	3.79	.34	11.32	.4
APPEL	2	47AF2S	8/14	2020	0740	67.96	2.25	13.6	0	0	67.96	2.25
APPEL	3	51AT3P	8/15	0801	1156	15.91	1.72	258.79	7.78	1.18	23.69	1.25
APPEL	3	51AT3A	8/15	0801	1156	2.61	.19	258.73	0	0	2.61	.14
APPEL	4	51AT4P	8/15	0759	1200	37.36	1.83	1.97	<7.03	0	37.36	1.45
APPEL	4	51AT4A	8/15	0759	1200	4.37	.56	1.97	0	0	4.37	.54
APPEL	3	52AT3P	8/15	1200	1555	26.22	2.47	265.51	7.71	1.70	33.93	1.79
APPEL	3	52AT3A	8/15	1200	1555	6.46	.47	265.51	0	0	6.46	.34
APPEL	4	52AT4P	8/15	1202	1556	43.14	2.09	1.91	<7.25	0	43.14	1.64
APPEL	4	52AT4A	8/15	1202	1556	9.32	.72	1.91	0	0	9.32	.66
APPEL	3	53AT3P	8/15	1558	1958	16.16	1.48	271.84	4.17	1.02	20.33	1.07
APPEL	3	53AT3A	8/15	1558	1958	3.2	.23	271.84	0	0	3.20	.17
APPEL	4	53AT4P	8/15	1557	1957	31.09	1.57	1.92	<7.21	0	31.09	1.27
APPEL	4	53AT4A	8/15	1557	1957	8.28	.68	1.92	0	0	8.28	.63
APPEL	3	54AT3P	8/15	2002	2356	8.45	.86	265.05	3.32	.59	11.77	.62
APPEL	3	54AT3A	8/15	2002	2356	1.85	.13	265.05	0	0	1.85	.1
APPEL	4	54AT4P	8/15	1959	2355	17.57	1.03	1.89	<7.33	0	17.57	.88
APPEL	4	54AT4A	8/15	1959	2355	32.91	1.66	1.89	0	0	32.91	1.33
APPEL	3	55AT3P	8/15	2359	0807	7.13	.79	549.43	3.66	.54	10.79	.57
APPEL	3	55AT3A	8/15	2359	0807	1.78	.13	549.43	0	0	1.78	.09
APPEL	4	55AT4P	8/15	2356	0801	15	.77	3.88	<3.57	0	15.00	.62
APPEL	4	55AT4A	8/15	2356	0801	2.71	.29	3.88	0	0	2.71	.28
APPEL	1	56AD1F	8/15	0808	2008	19.55	1.15	14.62	5.05	.74	24.60	.82
APPEL	1	56AD1S	8/15	0808	2008	5.82	.26	14.62	0	0	5.82	.26
APPEL	2	56AF2F	8/15	0808	2008	16.81	.99	14.4	5.20	.66	22.01	.74
APPEL	2	56AF2S	8/15	0808	2008	13.78	.51	14.4	0	0	13.78	.51
APPEL	1	57AD1F	8/15	2026	0803	7.58	.56	13.94	3.73	.34	11.31	.44
APPEL	1	57AD1S	8/15	2026	0803	9.08	.36	13.94	0	0	9.08	.36
APPEL	2	57AF2F	8/15	2026	0803	7.35	.5	13.94	3.52	.33	10.87	.38
APPEL	2	57AF2S	8/15	2026	0803	2.9	.19	13.94	0	0	2.90	.19
APPEL	3	61AT3P	8/16	0822	1155	17.43	1.65	234.5	5.20	1.13	22.63	1.2
APPEL	3	61AT3A	8/16	0822	1155	5.25	.38	234.5	0	0	5.25	.28
APPEL	4	61AT4P	8/16	0802	1158	32.38	1.63	1.93	<7.18	0	32.38	1.31
APPEL	4	61AT4A	8/16	0802	1158	5.28	.59	1.93	0	0	5.28	.57
APPEL	3	62AT3P	8/16	1157	1557	21.67	1.82	265.73	3.25	1.25	24.92	1.32
APPEL	3	62AT3A	8/16	1157	1557	4.03	.29	265.73	0	0	4.03	.21
APPEL	4	62AT4P	8/16	1159	1559	37.69	1.85	1.99	<6.96	0	37.69	1.46
APPEL	4	62AT4A	8/16	1159	1559	6.28	.6	1.99	0	0	6.28	.57
APPEL	3	63AT3P	8/16	1558	1958	23.95	1.95	279.22	2.90	1.34	26.85	1.42
APPEL	3	63AT3A	8/16	1558	1958	4.02	.29	279.22	0	0	4.02	.21
APPEL	4	63AT4P	8/16	1601	1959	37.42	1.85	1.9	<7.29	0	37.42	1.47
APPEL	4	63AT4A	8/16	1601	1959	5.63	.6	1.9	0	0	5.63	.58

APPEL	3	64AT3A	8/16	2000	2358	2.76	.21	270.92	0	0	2.76	.15
APPEL	4	64AT4P	8/16	2000	2357	23.88	1.28	1.88	<7.37	0	23.88	1.06
APPEL	4	64AT4A	8/16	2000	2357	3.51	.56	1.88	0	0	3.51	.55
APPEL	3	65AT3P	8/16	2400	0759	12.51	1.09	536.31	2.49	.75	15.00	.79
APPEL	3	65AT3A	8/16	2400	0759	1.96	.14	536.31	0	0	1.96	.1
APPEL	4	65AT4P	8/16	2358	0803	20.62	1	4.03	<3.44	0	20.62	.78
APPEL	4	65AT4A	8/16	2358	0803	3.18	.31	4.03	0	0	3.18	.29
APPEL	1	66AD1F	8/16	0814	2000	16.32	.9	14.12	3.69	.60	20.01	.67
APPEL	1	66AD1S	8/16	0814	2000	3.36	.19	14.12	0	0	3.36	.19
APPEL	2	66AF2F	8/16	0814	2000	16.82	.92	14.12	3.52	.61	20.34	.69
APPEL	2	66AF2S	8/16	0814	2000	3.94	.21	14.12	0	0	3.94	.21
APPEL	1	67AD1F	8/16	2020	0745	11.57	.65	13.64	2.62	.43	14.19	.49
APPEL	1	67AD1S	8/16	2020	0745	4.21	.22	13.64	0	0	4.21	.22
APPEL	2	67AF2F	8/16	2020	0745	11.88	.67	13.55	2.64	.44	14.52	.5
APPEL	2	67AF2S	8/16	2020	0745	4.15	.21	14.55	0	0	4.15	.21
APPEL	3	71AT3P	8/17	0803	1154	23.19	1.93	258.64	3.34	1.33	26.53	1.4
APPEL	3	71AT3A	8/17	0803	1154	3.85	.28	258.64	0	0	3.85	.2
APPEL	4	71AT4P	8/17	0803	1155	34.97	1.73	1.93	<7.18	0	34.97	1.38
APPEL	4	71AT4A	8/17	0803	1155	6.06	.61	1.93	0	0	6.06	.58
APPEL	3	72AT3P	8/17	1157	1557	25.85	2.09	264.23	3.00	1.44	28.85	1.52
APPEL	3	72AT3A	8/17	1157	1557	3.98	.29	264.23	0	0	3.98	.21
APPEL	4	72AT4P	8/17	1156	1556	38.01	1.86	1.96	<7.07	0	38.01	1.47
APPEL	4	72AT4A	8/17	1156	1556	6.17	.61	1.96	0	0	6.17	.58
APPEL	3	73AT3P	8/17	1604	1959	17.8	1.44	274.86	1.95	.99	19.75	1.04
APPEL	3	73AT3A	8/17	1604	1959	3.79	.28	274.86	0	0	3.79	.2
APPEL	4	73AT4P	8/17	1600	1959	31.1	1.57	1.91	<7.25	0	31.10	1.27
APPEL	4	73AT4A	8/17	1600	1959	6.49	.63	1.91	0	0	6.49	.6
APPEL	3	74AT3P	8/17	2009	2359	11.13	.95	260.52	1.83	.65	12.96	.69
APPEL	3	74AT3A	8/17	2009	2359	2.35	.17	260.52	0	0	2.35	.12
APPEL	4	74AT4P	8/17	2004	2358	14.97	.81	1.87	<7.41	0	14.97	.81
APPEL	4	74AT4A	8/17	2004	2358	6.79	.61	1.87	0	0	6.79	.61
APPEL	3	75AT3P	8/17	2400	0800	8	.83	534.44	3.46	.57	11.46	.6
APPEL	3	75AT3A	8/17	2400	0800	2.24	.16	534.44	0	0	2.24	.12
APPEL	4	75AT4P	8/17	2359	0800	17.27	.86	3.85	<3.6	0	17.27	.69
APPEL	4	75AT4A	8/17	2359	0800	4.43	.32	3.95	0	0	4.43	.32
APPEL	1	76AD1F	8/17	0759	1945	16.9	.88	14.24	2.55	.58	19.45	.66
APPEL	1	76AD1S	8/17	0759	1945	4.04	.21	14.24	0	0	4.04	.21
APPEL	2	76AF2F	8/17	0759	1945	17.63	.92	14.12	2.86	.61	20.49	.69
APPEL	2	76AF2S	8/17	0759	1945	2.29	.17	14.12	0	0	2.29	.17
APPEL	1	77AD1F	8/17	2000	0800	7.49	.48	14.4	2.89	.31	10.38	.36
APPEL	1	77AD1S	8/17	2000	0800	8.79	.35	14.4	0	0	8.79	.35
APPEL	2	77AF2F	8/17	2000	0800	8.12	.5	14.24	2.84	.33	10.96	.38
APPEL	2	77AF2S	8/17	2000	0800	4.37	.22	14.24	0	0	4.37	.22
APPEL	3	81AT3P	8/18	0803	1201	17.72	1.79	264.99	6.97	1.23	24.69	1.3
APPEL	3	81AT3A	8/18	0803	1201	3.59	.26	264.99	0	0	3.59	.19
APPEL	4	81AT4P	8/18	0801	1159	51.41	2.44	1.98	<6.99	0	51.41	1.89
APPEL	4	81AT4A	8/18	0801	1159	7.27	.64	1.98	0	0	7.27	.6
APPEL	3	82AT3P	8/18	1202	1602	20.72	1.83	268.72	4.46	1.26	25.18	1.33
APPEL	3	82AT3A	8/18	1202	1602	3.63	.26	268.72	0	0	3.63	.19
APPEL	4	82AT4P	8/18	1200	1600	33.06	1.65	1.96	<7.07	0	33.06	1.32
APPEL	4	82AT4A	8/18	1200	1600	5.87	.6	1.96	0	0	5.87	.57
APPEL	3	83AT3P	8/18	1604	2000	15.6	1.37	267.31	3.29	.94	18.89	1
APPEL	3	83AT3A	8/18	1604	2000	2.8	.21	267.31	0	0	2.80	.15
APPEL	4	83AT4P	8/18	1601	1956	32.15	1.64	1.77	<7.82	0	32.15	1.33
APPEL	4	83AT4A	8/18	1601	1956	6.72	.67	1.77	0	0	6.72	.64
APPEL	3	84AT3P	8/18	2005	2400	13.5	1.22	257.19	3.22	.84	16.72	.88
APPEL	3	84AT3A	8/18	2005	2400	2.64	.19	257.19	0	0	2.64	.14
APPEL	4	84AT4P	8/18	1959	2400	53.02	2.52	1.92	<7.21	0	53.02	1.95
APPEL	4	84AT4A	8/18	1959	2400	4.9	.58	1.92	0	0	4.90	.56
APPEL	3	85AT3P	8/18	0116	0754	10.15	.95	443.14	2.85	.65	13.00	.69
APPEL	3	85AT3A	8/18	0116	0754	3.02	.22	443.14	0	0	3.02	.16
APPEL	4	85AT4P	8/18	2403	0754	19.92	.98	3.77	<3.67	0	19.92	.77
APPEL	4	85AT4A	8/18	2403	0754	4.35	.35	3.77	0	0	4.35	.33
APPEL	1	86AD1F	8/18	0820	2000	11.93	.77	14	4.36	.53	16.29	.56
APPEL	1	86AD1S	8/18	0820	2000	3.22	.19	14	0	0	.57	.08
APPEL	2	86AF2F	8/18	0820	2000	14.29	.84	13.94	4.26	.56	18.55	.63

APPEL	4	CONF 4S	8/18	0820	2000	5.46	.25	13.94	0	0	1.04	.09
APPEL	1	87AD1F	8/18	2022	0757	7.83	.48	13.9	2.66	.31	10.49	.37
APPEL	1	87AD1S	8/18	2022	0757	2.29	.17	13.9	0	0	2.29	.17
APPEL	2	87AF2F	8/18	2022	0757	8.82	.54	13.9	2.81	.35	11.63	.41
APPEL	2	87AF2S	8/18	2022	0757	7.72	.32	13.9	0	0	7.72	.32
APPEL	3	91AT3P	8/19	0756	1201	17.69	1.63	274.04	4.74	1.12	22.43	1.18
APPEL	3	91AT3A	8/19	0756	1201	3.51	.26	274.04	0	0	3.51	.26
APPEL	4	91AT4P	8/19	0755	1159	32.41	1.62	1.99	<6.96	0	32.41	1.3
APPEL	4	91AT4A	8/19	0755	1159	6.93	.63	1.99	0	0	6.93	.63
APPEL	3	92AT3P	8/19	1204	1600	20.19	1.8	265.71	4.59	1.24	24.78	1.31
APPEL	3	92AT3A	8/19	1204	1600	4.2	.3	265.71	0	0	4.20	.3
APPEL	4	92AT4P	8/19	1200	1600	38.23	1.88	1.92	<7.21	0	38.23	1.49
APPEL	4	92AT4A	8/19	1200	1600	6.67	.63	1.92	0	0	6.67	.6
APPEL	3	93AT3P	8/19	1602	2000	10.76	.96	275.41	2.45	.66	13.21	.7
APPEL	3	93AT3A	8/19	1602	2000	2.96	.22	275.41	0	0	2.96	.16
APPEL	4	93AT4P	8/19	1601	2000	20.92	1.15	1.95	<7.1	0	20.92	.96
APPEL	4	93AT4A	8/19	1601	2000	4.15	.55	1.95	0	0	4.15	.54
APPEL	3	94AT3P	8/19	2004	2359	11.14	1.03	264.58	3.13	.71	14.27	.75
APPEL	3	94AT3A	8/19	2004	2359	2.87	.21	264.58	0	0	2.87	.15
APPEL	4	94AT4P	8/19	2001	2358	21.53	1.18	1.9	<7.29	0	21.53	.99
APPEL	4	94AT4A	8/19	2001	2358	5.95	.62	1.9	0	0	5.95	.59
APPEL	3	95AT3P	8/19	2401	0800	11.34	1.06	539.16	3.31	.73	14.65	.77
APPEL	3	95AT3A	8/19	2401	0800	2.68	.19	539.16	0	0	2.68	.14
APPEL	4	95AT4P	8/19	2359	0800	21.9	1.06	3.85	<3.6	0	21.90	.83
APPEL	4	95AT4A	8/19	2359	0800	4.29	.35	3.85	0	0	4.29	.32
APPEL	1	96AD1F	8/19	0829	2000	12.77	.73	13.82	3.34	.48	16.11	.55
APPEL	1	96AD1S	8/19	0829	2000	19.44	.69	13.82	0	0	19.44	.69
APPEL	2	96AF2F	8/19	0829	2000	12.85	.76	13.76	3.88	.50	16.73	.57
APPEL	2	96AF2S	8/19	0829	2000	11.1	.42	13.76	0	0	11.10	.42
APPEL	1	97AD1F	8/19	2019	0802	10.06	.67	14.06	3.28	.44	13.34	.46
APPEL	1	97AD1S	8/19	2019	0802	8.7	.35	14.06	0	0	8.70	.35
APPEL	2	97AF2F	8/19	2019	0802	10.1	.61	14.06	3.36	.40	13.46	.46
APPEL	2	97AF2S	8/19	2019	0802	5.48	.25	14.06	0	0	5.48	.25
APPEL	3	101AT3P	8/20	0802	1201	23.88	2.54	242.25	11.04	1.75	34.92	1.84
APPEL	3	101AT3A	8/20	0802	1201	5.98	.44	242.25	0	0	5.98	.32
APPEL	4	101AT4P	8/20	0800	1200	34.49	2.05	1.99	7.97	1.27	42.46	1.61
APPEL	4	101AT4A	8/20	0800	1200	7.24	.64	1.99	0	0	7.24	.6
APPEL	3	102AT3P	8/20	1205	1557	23.91	2.12	269.91	5.21	1.46	29.12	1.54
APPEL	3	102AT3A	8/20	1205	1557	5.05	.37	269.91	0	0	5.05	.27
APPEL	4	102AT4P	8/20	1201	1558	29.05	1.49	1.9	<7.29	0	29.05	1.21
APPEL	4	102AT4A	8/20	1201	1558	8.74	.7	1.9	0	0	8.74	.65
APPEL	3	103AT3P	8/20	1558	1958	14.04	1.28	261.24	3.51	.88	17.55	.93
APPEL	3	103AT3A	8/20	1558	1958	3.13	.23	261.24	0	0	3.13	.17
APPEL	4	103AT4P	8/20	1559	1959	23.91	1.27	1.92	<7.21	0	23.91	1.05
APPEL	4	103AT4A	8/20	1559	1959	4.38	.57	1.92	0	0	4.38	.55
APPEL	3	104AT3P	8/20	2003	2354	12.41	1.2	261.65	4.10	.83	16.51	.87
APPEL	3	104AT3A	8/20	2003	2354	3.28	.23	261.65	0	0	3.28	.17
APPEL	4	104AT4P	8/20	2000	2352	27.9	1.45	1.86	<7.45	0	27.90	1.18
APPEL	4	104AT4A	8/20	2000	2352	5.05	.6	1.86	0	0	5.05	.58
APPEL	3	105AT3P	8/20	2357	0802	13.11	1.34	509.73	5.25	.92	18.36	.97
APPEL	3	105AT3A	8/20	2357	0802	<.1	.22	509.73	0	0	<.1	.22
APPEL	4	105AT4P	8/20	2357	0802	18.5	1.12	3.91	4.82	.70	23.32	.87
APPEL	4	105AT4A	8/20	2357	0802	5.27	.38	3.91	0	0	5.27	.34
APPEL	1	106AD1F	8/20	0824	2000	15.06	.92	14.04	5.37	.61	20.43	.69
APPEL	1	106AD1S	8/20	0824	2000	7.42	.31	14.04	0	0	7.42	.31
APPEL	2	106AF2F	8/20	0824	2000	15.92	.96	14.04	5.56	.64	21.48	.72
APPEL	2	106AF2S	8/20	0824	2000	4.5	.23	14.04	0	0	4.50	.23
APPEL	1	107AD1F	8/20	2019	0802	10.23	.67	13.91	4.47	.44	14.70	.5
APPEL	1	107AD1S	8/20	2019	0802	5.98	.27	13.91	0	0	5.98	.27
APPEL	2	107AF2F	8/20	2019	0802	11.16	.72	14	4.66	.47	15.82	.54
APPEL	2	107AF2S	8/20	2019	0802	6.25	.28	14	0	0	6.25	.28

* BAD DATA

Table 15

CARBON STUDY FIELD SAMPLES

A B GROUP	SAMPLE SAMPLE No.	START DATE	START TIME (PDT)	STOP TIME (PDT)	ORG. C LOADING UgC/m3	ORG. C ERROR UgC/m3	VOLUME m3	ELEM C LOADING UgC/m3	ELEM C ERROR UgC/m3	TOTAL C LOADING UgC/m3	TOT C. ERROR UgC/m3
APPEL 1	26AD1F	8/12	0800	1958	16.52	1.05	14.68	5.59	.70	22.11	.74
APPEL 1	26AD1S	8/12	0800	1958	11.15	.42	14.68	0	0	11.15	.42
APPEL 1	27AD1F	8/12	2024	0751	10.53	.73	13.74	5.60	.48	16.13	.55
APPEL 1	27AD1S	8/12	2024	0751	16.59	.6	13.74	0	0	16.59	.6
APPEL 1	36AD1F	8/13	0803	2003	14.94	.93	14.9	5.63	.62	20.57	.69
APPEL 1	36AD1S	8/13	0803	2003	8.08	.33	14.9	0	0	8.08	.33
APPEL 1	37AD1F	8/13	2030	0745	9.13	.61	13.44	4.23	.40	13.36	.46
APPEL 1	37AD1S	8/13	2030	0745	3.12	.19	13.44	0	0	3.12	.19
APPEL 1	46AD1F	8/14	0800	2000	18.2	1.06	14.4	5.35	.71	23.55	.79
APPEL 1	46AD1S	8/14	0800	2000	5.51	.25	14.4	0	0	5.51	.25
APPEL 1	47AD1F	8/14	2020	0740	7.52	.52	13.72	3.73	.34	11.25	.39
APPEL 1	47AD1S	8/14	2020	0740	8.18	.34	13.72	0	0	8.18	.34
APPEL 1	56AD1F	8/15	0808	2008	19.55	1.15	14.62	5.05	.74	24.60	.82
APPEL 1	56AD1S	8/15	0808	2008	5.82	.26	14.62	0	0	5.82	.26
APPEL 1	57AD1F	8/15	2026	0803	7.58	.56	13.94	3.73	.34	11.31	.44
APPEL 1	57AD1S	8/15	2026	0803	9.08	.36	13.94	0	0	9.08	.36
APPEL 1	66AD1F	8/16	0814	2000	16.32	.9	14.12	3.69	.60	20.01	.67
APPEL 1	66AD1S	8/16	0814	2000	3.36	.19	14.12	0	0	3.36	.19
APPEL 1	67AD1F	8/16	2020	0745	11.57	.65	13.64	2.62	.43	14.19	.49
APPEL 1	67AD1S	8/16	2020	0745	4.21	.22	13.64	0	0	4.21	.22
APPEL 1	76AD1F	8/17	0759	1945	16.9	.88	14.24	2.55	.58	19.45	.66
APPEL 1	76AD1S	8/17	0759	1945	4.04	.21	14.24	0	0	4.04	.21
APPEL 1	77AD1F	8/17	2000	0800	7.49	.48	14.4	2.89	.31	10.38	.36
APPEL 1	77AD1S	8/17	2000	0800	8.79	.35	14.4	0	0	8.79	.35
APPEL 1	86AD1F	8/18	0820	2000	11.93	.77	14	4.36	.53	16.29	.56
APPEL 1	86AD1S	8/18	0820	2000	3.22	.19	14	0	0	.57	.08
APPEL 1	87AD1F	8/18	2022	0757	7.83	.48	13.9	2.66	.31	10.49	.37
APPEL 1	87AD1S	8/18	2022	0757	2.29	.17	13.9	0	0	2.29	.17
APPEL 1	96AD1F	8/19	0829	2000	12.77	.73	13.82	3.34	.48	16.11	.55
APPEL 1	96AD1S	8/19	0829	2000	19.44	.69	13.82	0	0	19.44	.69
APPEL 1	97AD1F	8/19	2019	0802	10.06	.67	14.06	3.28	.44	13.34	.46
APPEL 1	97AD1S	8/19	2019	0802	8.7	.35	14.06	0	0	8.70	.35
APPEL 1	106AD1F	8/20	0824	2000	15.06	.92	14.04	5.37	.61	20.43	.69
APPEL 1	106AD1S	8/20	0824	2000	7.42	.31	14.04	0	0	7.42	.31
APPEL 1	107AD1F	8/20	2019	0802	10.23	.67	13.91	4.47	.44	14.70	.5
APPEL 1	107AD1S	8/20	2019	0802	5.98	.27	13.91	0	0	5.98	.27
APPEL 2	26AF2F	8/12	0800	1958	16.89	1.01	14.49	5.39	.67	22.28	.75
APPEL 2	26AF2S	8/12	0800	1958	11.43	.43	14.49	0	0	11.43	.43
APPEL 2	27AF2F	8/12	2024	0751	9.01	.62	13.74	4.57	.41	13.58	.47
APPEL 2	27AF2S	8/12	2024	0751	3.25	.2	13.74	0	0	3.25	.2
APPEL 2	36AF2F	8/13	0803	2003	15.56	.96	14.4	5.79	.64	21.35	.72
APPEL 2	36AF2S	8/13	0803	2003	5.18	.24	14.4	0	0	5.18	.24
APPEL 2	37AF2F	8/13	2028	0745	10.37	.67	13.48	4.33	.44	14.70	.51
APPEL 2	37AF2S	8/13	2028	0745	2.46	.18	13.48	0	0	2.46	.18
APPEL 2	46AF2F	8/14	0800	2000	19.12	1.1	14.4	5.54	.74	24.66	.82
APPEL 2	46AF2S	8/14	0800	2000	7.08	.3	14.4	0	0	7.08	.3
APPEL 2	47AF2F	8/14	2020	0740	7.53	.52	13.6	3.79	.34	11.32	.4
APPEL 2	47AF2S	8/14	2020	0740	67.96	2.25	13.6	0	0	67.96	2.25
APPEL 2	56AF2F	8/15	0808	2008	16.81	.99	14.4	5.20	.66	22.01	.74
APPEL 2	56AF2S	8/15	0808	2008	13.78	.51	14.4	0	0	13.78	.51
APPEL 2	57AF2F	8/15	2026	0803	7.35	.5	13.94	3.52	.33	10.87	.38
APPEL 2	57AF2S	8/15	2026	0803	2.9	.19	13.94	0	0	2.90	.19
APPEL 2	66AF2F	8/16	0814	2000	16.82	.92	14.12	3.52	.61	20.34	.69
APPEL 2	66AF2S	8/16	0814	2000	3.94	.21	14.12	0	0	3.94	.21
APPEL 2	67AF2F	8/16	2020	0745	11.88	.67	13.55	2.64	.44	14.52	.5
APPEL 2	67AF2S	8/16	2020	0745	4.15	.21	14.55	0	0	4.15	.21
APPEL 2	76AF2F	8/17	0759	1945	17.63	.92	14.12	2.84	.41	20.49	.70

APPEL	2	76AF2S	8/17	0759	1945	2.29	.17	14.12	0	0	2.29	.17
APPEL	2	77AF2F	8/17	2000	0800	8.12	.5	14.24	2.84	.33	10.96	.38
APPEL	2	77AF2S	8/17	2000	0800	4.37	.22	14.24	0	0	4.37	.22
APPEL	2	86AF2F	8/18	0820	2000	14.29	.84	13.94	4.26	.56	18.55	.63
APPEL	2	86AF2S	8/18	0820	2000	5.46	.25	13.94	0	0	1.04	.09
APPEL	2	87AF2F	8/18	2022	0757	8.82	.54	13.9	2.81	.35	11.63	.41
APPEL	2	87AF2S	8/18	2022	0757	7.72	.32	13.9	0	0	7.72	.32
APPEL	2	96AF2F	8/19	0829	2000	12.85	.76	13.76	3.88	.50	16.73	.57
APPEL	2	96AF2S	8/19	0829	2000	11.1	.42	13.76	0	0	11.10	.42
APPEL	2	97AF2F	8/19	2019	0802	10.1	.61	14.06	3.36	.40	13.46	.46
APPEL	2	97AF2S	8/19	2019	0802	5.48	.25	14.06	0	0	5.48	.25
APPEL	2	106AF2F	8/20	0824	2000	15.92	.96	14.04	5.56	.64	21.48	.72
APPEL	2	106AF2S	8/20	0824	2000	4.5	.23	14.04	0	0	4.50	.23
APPEL	2	107AF2F	8/20	2019	0802	11.16	.72	14	4.66	.47	15.82	.54
APPEL	2	107AF2S	8/20	2019	0802	6.25	.28	14	0	0	6.25	.28
APPEL	3	21AT3P	8/12	0800	1157	18.79	2.08	266.83	9.84	1.43	28.63	1.51
APPEL	3	21AT3A	8/12	0800	1157	5.04	.37	266.83	0	0	5.04	.27
APPEL	3	22AT3P	8/12	1218	1553	22.88	2.09	242.06	5.91	1.44	28.79	1.52
APPEL	3	22AT3A	8/12	1218	1553	5.51	.4	242.06	0	0	5.51	.29
APPEL	3	23AT3P	8/12	1554	1953	12.94	1.2	281.03	3.47	.82	16.41	.87
APPEL	3	23AT3A	8/12	1554	1953	3.56	.26	281.03	0	0	3.56	.19
APPEL	3	24AT3P	8/12	1955	2355	11.08	1.15	270.21	4.76	.79	15.84	.84
APPEL	3	24AT3A	8/12	1955	2355	2.55	.18	270.21	0	0	2.55	.13
APPEL	3	25AT3P	8/12	2357	0810	7.69	.94	542.77	5.22	.65	12.91	.68
APPEL	3	25AT3A	8/12	2357	0810	2.35	.17	542.77	0	0	2.35	.12
APPEL	3	31AT3P	8/13	0815	1155	16.45	1.82	249.19	8.65	1.26	25.10	1.33
APPEL	3	31AT3A	8/13	0815	1155	4.1	.3	249.19	0	0	4.10	.22
APPEL	3	32AT3P	8/13	1157	1158	17.99	1.75	271.34	6.04	1.20	24.03	1.27
APPEL	3	32AT3A	8/13	1157	1158	3.74	.28	271.34	0	0	3.74	.2
APPEL	3	33AT3P	8/13	1600	2000	19.01	1.72	273.2	4.63	1.18	23.64	1.25
APPEL	3	33AT3A	8/13	1600	2000	3.75	.28	273.2	0	0	3.75	.2
APPEL	3	34AT3P	8/13	2001	2401	10.77	1.09	273.2	4.23	.75	15.00	.79
APPEL	3	34AT3A	8/13	2001	2401	2.48	.18	273.2	0	0	2.48	.13
APPEL	3	35AT3P	8/13	2403	0804	7.71	.88	544.82	4.40	.61	12.11	.64
APPEL	3	35AT3A	8/13	2403	0804	1.74	.13	544.82	0	0	1.74	.09
APPEL	3	41AT3P	8/14	0806	1150	18.47	1.85	252.2	6.96	1.27	25.43	1.34
APPEL	3	41AT3A	8/14	0806	1150	6.2	.45	252.2	0	0	6.20	.33
APPEL	3	42AT3P	8/14	1153	1157	21.54	1.98	273.19	5.70	1.36	27.24	1.44
APPEL	3	42AT3A	8/14	1153	1157	5.22	.38	279.19	0	0	5.22	.28
APPEL	3	43AT3P	8/14	1559	1959	22.51	2.02	273.2	5.32	1.39	27.83	1.47
APPEL	3	43AT3A	8/14	1559	1959	5.2	.38	273.2	0	0	5.20	.28
APPEL	3	44AT3P	8/14	2002	2358	11.26	1.11	267.31	4.01	.76	15.27	.81
APPEL	3	44AT3A	8/14	2002	2358	2.22	.16	267.31	0	0	2.22	.12
APPEL	3	45AT3P	8/14	2359	0759	5.66	.69	549.39	3.76	.47	9.42	.5
APPEL	3	45AT3A	8/14	2359	0759	1.55	.11	549.39	0	0	1.55	.08
APPEL	3	51AT3P	8/15	0801	1156	15.91	1.72	258.73	7.78	1.18	23.69	1.25
APPEL	3	51AT3A	8/15	0801	1156	2.61	.19	258.73	0	0	2.61	.14
APPEL	3	52AT3P	8/15	1200	1553	26.22	2.47	265.51	7.71	1.70	33.93	1.79
APPEL	3	52AT3A	8/15	1200	1553	6.46	.47	265.51	0	0	6.46	.34
APPEL	3	53AT3P	8/15	1558	1958	16.16	1.48	271.84	4.17	1.02	20.33	1.07
APPEL	3	53AT3A	8/15	1558	1958	3.2	.23	271.84	0	0	3.20	.17
APPEL	3	54AT3P	8/15	2002	2356	8.45	.86	265.05	3.32	.59	11.77	.62
APPEL	3	54AT3A	8/15	2002	2356	1.85	.13	265.05	0	0	1.85	.1
APPEL	3	55AT3P	8/15	2359	0807	7.13	.79	549.43	3.66	.54	10.79	.57
APPEL	3	55AT3A	8/15	2359	0807	1.78	.13	549.43	0	0	1.78	.09
APPEL	3	61AT3P	8/16	0822	1155	17.43	1.65	234.5	5.20	1.13	22.63	1.2
APPEL	3	61AT3A	8/16	0822	1155	5.25	.38	234.5	0	0	5.25	.28
APPEL	3	62AT3P	8/16	1157	1557	21.67	1.82	265.73	3.25	1.25	24.92	1.32
APPEL	3	62AT3A	8/16	1157	1557	4.03	.29	265.73	0	0	4.03	.21
APPEL	3	63AT3P	8/16	1558	1958	23.95	1.95	279.22	2.90	1.34	26.85	1.42
APPEL	3	63AT3A	8/16	1558	1958	4.02	.29	279.22	0	0	4.02	.21
APPEL	3	64AT3P	8/16	2000	2358	12.5	1.1	270.92	2.74	.76	15.24	.8
APPEL	3	64AT3A	8/16	2000	2358	2.76	.21	270.92	0	0	2.76	.15
APPEL	3	65AT3P	8/16	2400	0759	12.51	1.09	536.31	2.49	.75	15.00	.79
APPEL	3	65AT3A	8/16	2400	0759	1.96	.14	536.31	0	0	1.96	.1
APPEL	3	71AT3P	8/17	0803	1154	23.19	1.93	258.64	3.34	1.33	26.53	1.4

APPEL	4	44A14A	8/14	2000	2358	4.74	.58	1.9	0	0	4.74	.56
APPEL	4	45AT4P	8/14	2358	0758	14.9	.76	3.84	<3.61	0	14.90	.61
APPEL	4	45AT4A	8/14	2358	0758	15.57	.79	3.84	0	0	15.57	.63
APPEL	4	51AT4P	8/15	0759	1200	37.36	1.83	1.97	<7.03	0	37.36	1.45
APPEL	4	51AT4A	8/15	0759	1200	4.37	.56	1.97	0	0	4.37	.54
APPEL	4	52AT4P	8/15	1202	1556	43.14	2.09	1.91	<7.25	0	43.14	1.64
APPEL	4	52AT4A	8/15	1202	1556	9.32	.72	1.91	0	0	9.32	.66
APPEL	4	53AT4P	8/15	1557	1957	31.09	1.57	1.92	<7.21	0	31.09	1.27
APPEL	4	53AT4A	8/15	1557	1957	8.28	.68	1.92	0	0	8.28	.63
APPEL	4	54AT4P	8/15	1959	2355	17.57	1.03	1.89	<7.33	0	17.57	.88
APPEL	4	54AT4A	8/15	1959	2355	32.91	1.66	1.89	0	0	32.91	1.33
APPEL	4	55AT4P	8/15	2356	0801	15	.77	3.88	<3.57	0	15.00	.62
APPEL	4	55AT4A	8/15	2356	0801	2.71	.29	3.88	0	0	2.71	.28
APPEL	4	61AT4P	8/16	0802	1158	32.38	1.63	1.93	<7.18	0	32.38	1.31
APPEL	4	61AT4A	8/16	0802	1158	5.28	.59	1.93	0	0	5.28	.57
APPEL	4	62AT4P	8/16	1159	1559	37.69	1.85	1.99	<6.96	0	37.69	1.46
APPEL	4	62AT4A	8/16	1159	1559	6.28	.6	1.99	0	0	6.28	.57
APPEL	4	63AT4P	8/16	1601	1959	37.42	1.85	1.9	<7.29	0	37.42	1.47
APPEL	4	63AT4A	8/16	1601	1959	5.63	.6	1.9	0	0	5.63	.58
APPEL	4	64AT4P	8/16	2000	2357	23.88	1.28	1.88	<7.37	0	23.88	1.06
APPEL	4	64AT4A	8/16	2000	2357	3.51	.56	1.88	0	0	3.51	.55
APPEL	4	65AT4P	8/16	2358	0803	20.62	1	4.03	<3.44	0	20.62	.78
APPEL	4	65AT4A	8/16	2358	0803	3.18	.31	4.03	0	0	3.18	.29
APPEL	4	71AT4P	8/17	0803	1155	34.97	1.73	1.93	<7.18	0	34.97	1.38
APPEL	4	71AT4A	8/17	0803	1155	6.06	.61	1.93	0	0	6.06	.58
APPEL	4	72AT4P	8/17	1156	1556	38.01	1.86	1.96	<7.07	0	38.01	1.47
APPEL	4	72AT4A	8/17	1156	1556	6.17	.61	1.96	0	0	6.17	.58
APPEL	4	73AT4P	8/17	1600	1959	31.1	1.57	1.91	<7.25	0	31.10	1.27
APPEL	4	73AT4A	8/17	1600	1959	6.49	.63	1.91	0	0	6.49	.6
APPEL	4	74AT4P	8/17	2004	2358	14.97	.81	1.87	<7.41	0	14.97	.81
APPEL	4	74AT4A	8/17	2004	2358	6.79	.61	1.87	0	0	6.79	.61
APPEL	4	75AT4P	8/17	2359	0800	17.27	.86	3.85	<3.6	0	17.27	.69
APPEL	4	75AT4A	8/17	2359	0800	4.43	.32	3.95	0	0	4.43	.32
APPEL	4	81AT4P	8/18	0801	1159	51.41	2.44	1.98	<6.99	0	51.41	1.89
APPEL	4	81AT4A	8/18	0801	1159	7.27	.64	1.98	0	0	7.27	.6
APPEL	4	82AT4P	8/18	1200	1600	33.06	1.65	1.96	<7.07	0	33.06	1.32
APPEL	4	82AT4A	8/18	1200	1600	5.87	.6	1.96	0	0	5.87	.57
APPEL	4	83AT4P	8/18	1601	1956	32.15	1.64	1.77	<7.82	0	32.15	1.33
APPEL	4	83AT4A	8/18	1601	1956	6.72	.67	1.77	0	0	6.72	.64
APPEL	4	84AT4P	8/18	1959	2400	53.02	2.52	1.92	<7.21	0	53.02	1.95
APPEL	4	84AT4A	8/18	1959	2400	4.9	.58	1.92	0	0	4.90	.56
APPEL	4	85AT4P	8/18	2403	0754	19.92	.98	3.77	<3.67	0	19.92	.77
APPEL	4	85AT4A	8/18	2403	0754	4.35	.35	3.77	0	0	4.35	.33
APPEL	4	91AT4P	8/19	0755	1159	32.41	1.62	1.99	<6.96	0	32.41	1.3
APPEL	4	91AT4A	8/19	0755	1159	6.93	.63	1.99	0	0	6.93	.63
APPEL	4	92AT4P	8/19	1200	1600	38.23	1.88	1.92	<7.21	0	38.23	1.49
APPEL	4	92AT4A	8/19	1200	1600	6.67	.63	1.92	0	0	6.67	.6
APPEL	4	93AT4P	8/19	1601	2000	20.92	1.15	1.95	<7.1	0	20.92	.96
APPEL	4	93AT4A	8/19	1601	2000	4.15	.55	1.95	0	0	4.15	.54
APPEL	4	94AT4P	8/19	2001	2358	21.53	1.18	1.9	<7.29	0	21.53	.99
APPEL	4	94AT4A	8/19	2001	2358	5.95	.62	1.9	0	0	5.95	.59
APPEL	4	95AT4P	8/19	2359	0800	21.9	1.06	3.85	<3.6	0	21.90	.83
APPEL	4	95AT4A	8/19	2359	0800	4.29	.35	3.85	0	0	4.29	.32
APPEL	4	101AT4P	8/20	0800	1200	34.49	2.05	1.99	7.97	1.27	42.46	1.61
APPEL	4	101AT4A	8/20	0800	1200	7.24	.64	1.99	0	0	7.24	.6
APPEL	4	102AT4P	8/20	1201	1558	29.05	1.49	1.9	<7.29	0	29.05	1.21
APPEL	4	102AT4A	8/20	1201	1558	8.74	.7	1.9	0	0	8.74	.65
APPEL	4	103AT4P	8/20	1559	1959	23.91	1.27	1.92	<7.21	0	23.91	1.05
APPEL	4	103AT4A	8/20	1559	1959	4.38	.57	1.92	0	0	4.38	.55
APPEL	4	104AT4P	8/20	2000	2352	27.9	1.45	1.86	<7.45	0	27.90	1.18
APPEL	4	104AT4A	8/20	2000	2352	5.05	.6	1.86	0	0	5.05	.58
APPEL	4	105AT4P	8/20	2357	0802	18.5	1.12	3.91	4.82	.70	23.32	.87
APPEL	4	105AT4A	8/20	2357	0802	5.27	.38	3.91	0	0	5.27	.34

APPEL	3	71AT3A	8/17	0803	1154	3.85	.28	258.64	0	0	3.85	.2
APPEL	3	72AT3P	8/17	1157	1557	25.85	2.09	264.23	3.00	1.44	28.85	1.52
APPEL	3	72AT3A	8/17	1157	1557	3.98	.29	264.23	0	0	3.98	.21
APPEL	3	73AT3P	8/17	1604	1959	17.8	1.44	274.86	1.95	.99	19.75	1.04
APPEL	3	73AT3A	8/17	1604	1959	3.79	.28	274.86	0	0	3.79	.2
APPEL	3	74AT3P	8/17	2009	2359	11.13	.95	260.52	1.83	.65	12.96	.69
APPEL	3	74AT3A	8/17	2009	2359	2.35	.17	260.52	0	0	2.35	.12
APPEL	3	75AT3P	8/17	2400	0800	8	.83	534.44	3.46	.57	11.46	.6
APPEL	3	75AT3A	8/17	2400	0800	2.24	.16	534.44	0	0	2.24	.12
APPEL	3	81AT3P	8/18	0803	1201	17.72	1.79	264.99	6.97	1.23	24.69	1.3
APPEL	3	81AT3A	8/18	0803	1201	3.59	.26	264.99	0	0	3.59	.19
APPEL	3	82AT3P	8/18	1202	1602	20.72	1.83	268.72	4.46	1.26	25.18	1.33
APPEL	3	82AT3A	8/18	1202	1602	3.63	.26	268.72	0	0	3.63	.19
APPEL	3	83AT3P	8/18	1604	2000	15.6	1.37	267.31	3.29	.94	18.89	1
APPEL	3	83AT3A	8/18	1604	2000	2.8	.21	267.31	0	0	2.80	.15
APPEL	3	84AT3P	8/18	2005	2400	13.5	1.22	257.19	3.22	.84	16.72	.88
APPEL	3	84AT3A	8/18	2005	2400	2.64	.19	257.19	0	0	2.64	.14
APPEL	3	85AT3P	8/18	0116	0754	10.15	.95	443.14	2.85	.65	13.00	.69
APPEL	3	85AT3A	8/18	0116	0754	3.02	.22	443.14	0	0	3.02	.16
APPEL	3	91AT3P	8/19	0756	1201	17.69	1.63	274.04	4.74	1.12	22.43	1.18
APPEL	3	91AT3A	8/19	0756	1201	3.51	.26	274.04	0	0	3.51	.26
APPEL	3	92AT3P	8/19	1204	1600	20.19	1.8	265.71	4.59	1.24	24.78	1.31
APPEL	3	92AT3A	8/19	1204	1600	4.2	.3	265.71	0	0	4.20	.3
APPEL	3	93AT3P	8/19	1602	2000	10.76	.96	275.41	2.45	.66	13.21	.7
APPEL	3	93AT3A	8/19	1602	2000	2.96	.22	275.41	0	0	2.96	.16
APPEL	3	94AT3P	8/19	2004	2359	11.14	1.03	264.58	3.13	.71	14.27	.75
APPEL	3	94AT3A	8/19	2004	2359	2.87	.21	264.58	0	0	2.87	.15
APPEL	3	95AT3P	8/19	2401	0800	11.34	1.06	539.16	3.31	.73	14.65	.77
APPEL	3	95AT3A	8/19	2401	0800	2.68	.19	539.16	0	0	2.68	.14
APPEL	3	101AT3P	8/20	0802	1201	23.88	2.54	242.25	11.04	1.75	34.92	1.84
APPEL	3	101AT3A	8/20	0802	1201	5.98	.44	242.25	0	0	5.98	.32
APPEL	3	102AT3P	8/20	1205	1557	23.91	2.12	269.91	5.21	1.46	29.12	1.54
APPEL	3	102AT3A	8/20	1205	1557	5.05	.37	269.91	0	0	5.05	.27
APPEL	3	103AT3P	8/20	1558	1958	14.04	1.28	261.24	3.51	.88	17.55	.93
APPEL	3	103AT3A	8/20	1558	1958	3.13	.23	261.24	0	0	3.13	.17
APPEL	3	104AT3P	8/20	2003	2354	12.41	1.2	261.65	4.10	.83	16.51	.87
APPEL	3	104AT3A	8/20	2003	2354	3.28	.23	261.65	0	0	3.28	.17
APPEL	3	105AT3P	8/20	2357	0802	13.11	1.34	509.73	5.25	.92	18.36	.97
APPEL	3	105AT3A	8/20	2357	0802	<.1	.22	509.73	0	0	<.1	.22
APPEL	4	21AT4P	8/12	0800	1157	36.64	2.13	1.97	7.57	1.33	44.21	1.66
APPEL	4	21AT4A	8/12	0800	1157	23.96	1.27	1.97	0	0	23.96	1.05
APPEL	4	22AT4P	8/12	1212	1555	45.34	2.2	1.78	<7.78	0	45.34	1.73
APPEL	4	22AT4A	8/12	1212	1555	15.67	.97	1.78	0	0	15.67	.85
APPEL	4	23AT4P	8/12	1605	1956	26.01	1.37	1.83	<7.57	0	26.01	1.13
APPEL	4	23AT4A	8/12	1605	1956	7.7	.68	1.83	0	0	7.70	.64
APPEL	4	24AT4P	8/12	1957	2358	28.65	1.47	1.93	<7.18	0	28.65	1.19
APPEL	4	24AT4A	8/12	1957	2358	9.22	.71	1.93	0	0	9.22	.65
APPEL	4	25AT4P	8/12	2400	0808	13.4	.91	3.9	4.96	.55	18.36	.72
APPEL	4	25AT4A	8/12	2400	0808	3.69	.32	3.9	0	0	3.69	.3
APPEL	4	31AT4P	8/13	0809	1159	40.27	1.97	1.88	<7.37	0	40.27	1.56
APPEL	4	31AT4A	8/13	0809	1159	9.79	.74	1.88	0	0	9.79	.68
APPEL	4	32AT4P	8/13	1200	1600	37.14	1.83	1.96	<7.07	0	37.14	1.45
APPEL	4	32AT4A	8/13	1200	1600	12.91	.84	1.96	0	0	12.91	.74
APPEL	4	33AT4P	8/13	1601	2001	35.21	1.75	1.92	<7.21	0	35.21	1.39
APPEL	4	33AT4A	8/13	1601	2001	9.69	.73	1.92	0	0	9.69	.67
APPEL	4	34AT4P	8/13	2002	2404	21.09	1.16	1.92	<7.21	0	21.09	.97
APPEL	4	34AT4A	8/13	2002	2404	7.5	.66	1.92	0	0	7.50	.62
APPEL	4	35AT4P	8/13	2406	0801	14.67	.91	3.8	3.67	.55	18.34	.72
APPEL	4	35AT4A	8/13	2406	0801	4.58	.36	3.8	0	0	4.58	.33
APPEL	4	41AT4P	8/14	0802	1154	41.84	2.04	1.9	<7.29	0	41.84	1.6
APPEL	4	41AT4A	8/14	0802	1154	9.89	.74	1.9	0	0	9.89	.68
APPEL	4	42AT4P	8/14	1155	1558	39.2	1.92	1.99	<6.96	0	39.20	1.51
APPEL	4	42AT4A	8/14	1155	1558	13.57	.85	1.99	0	0	13.57	.75
APPEL	4	43AT4P	8/14	1558	1958	41.21	2.01	1.9	<7.29	0	41.21	1.58
APPEL	4	43AT4A	8/14	1558	1958	6.63	.63	1.9	0	0	6.63	.6
APPEL	4	44AT4P	8/14	2000	2358	28.74	1.48	1.9	<7.29	0	28.74	1.2

VI. ANALYSIS OF ATMOSPHERIC RESULTS

A. Loss of Non-Volatile Fine Particles in the Alumina Denuder

To assess the efficiency of transmission of non-volatile, fine particles through the parallel-plate denuder of Sampler 1, C_g concentrations measured by the quartz filter of Sampler 1 are compared to those from Sampler 2 in a scatter diagram (Figure 9). The data sets are highly correlated, with a small intercept and a slope not significantly different from 1.0. Accordingly, no loss of non-volatile fine particles in the denuder is evident.

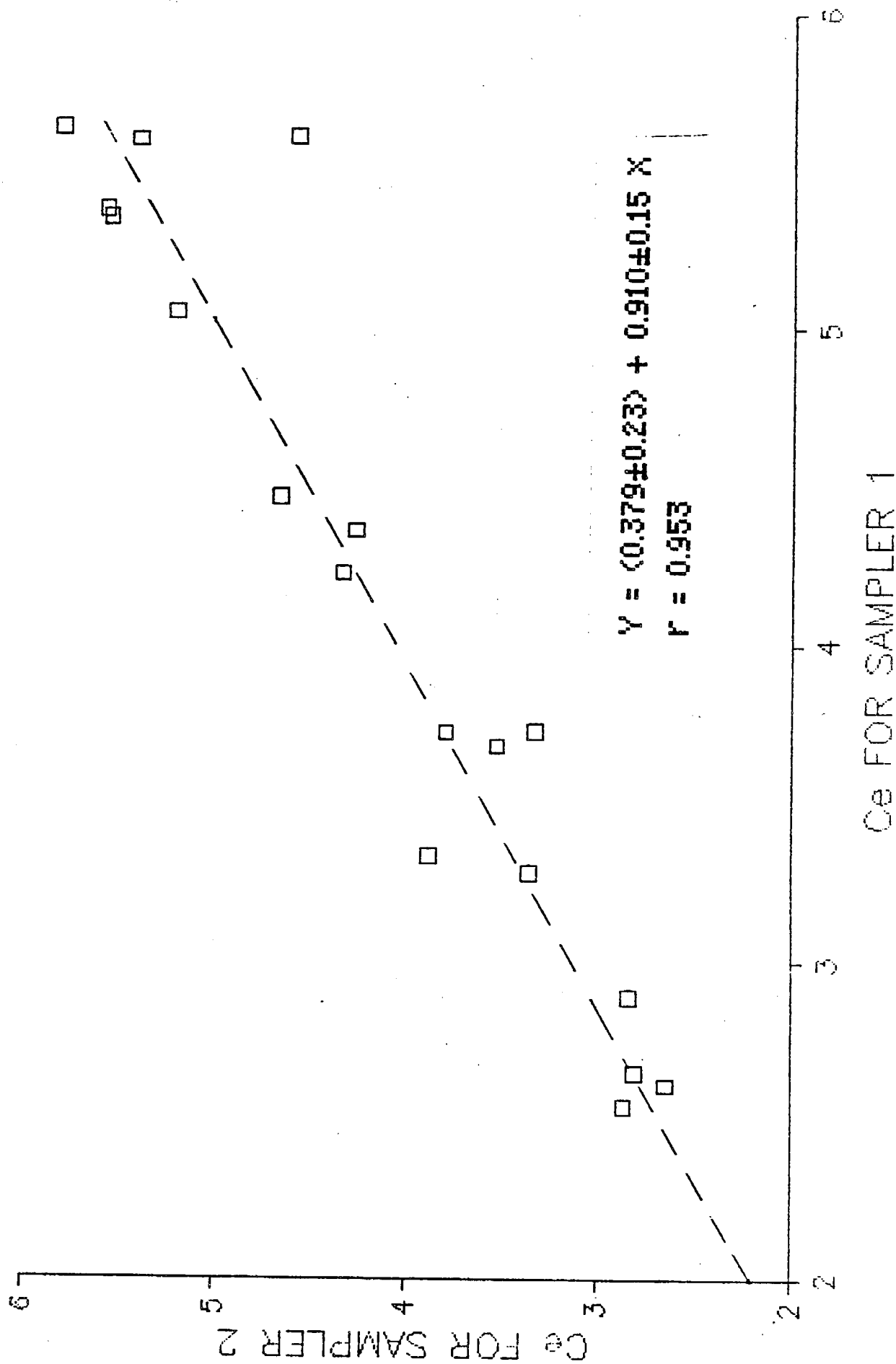
B. Organic Carbon Sampling with the FPC and LVFC Samplers

Table 16 compiles results for Sampler 1 and 2 which were being evaluated as fine particulate carbon (FPC) and low volatility fine carbon (LVFC) samplers, respectively. With both samplers, the ratio of Al_2O_3 to filter-collected carbon was quite variable, ranging from 0.13 to 1.5. On average about one third of the total collected carbon was retained on the Al_2O_3 and recovered with $MeCl_2$ for both samplers. Figure 10 compares the carbon recovered from the Al_2O_3 of the two samplers, showing low correlation between data sets. The scatter in this plot reflects the combined influence of errors in recovery of total carbon, enhancement in loss of organics from the filter of sampler 1 caused by the presence of the denuder, and higher efficiency of the sampler 1 Al_2O_3 because of H_2O removal by the denuder. Since carbon recovered from the filters of these samplers is not significantly different, loss of filter carbon cannot be contributing greatly to differences in carbon on the Al_2O_3 . If H_2O removal was the dominant factor, sampler 1 Al_2O_3 should always be higher than sampler 2 Al_2O_3 and especially so at night (i.e. for period 7). To assess the influence of atmospheric moisture on Al_2O_3 collection efficiency, Figure 11 shows a scatter diagram of the ratio of carbon on the Al_2O_3 of the two samplers against the mean relative humidity. No correlation is evident, indicating that analytical variability might be the predominant source of scatter in these results.

Comparing the total organic carbon recovered from the two samplers (i.e. filter plus Al_2O_3), there was no significant difference in recovered carbon. Thus, based on Table 16, and assuming that the denuder did not contribute to total carbon measurements on the filter by transfer of alumina, or other carbon-containing material, the denuder failed to remove a significant quantity of the vapor phase carbonaceous compounds present in the ambient air sample which could be trapped and recovered from the quartz filter and/or fluidized bed of alumina (eluting with $MeCl_2$). From the experiment detailed in Section IV E, it also seems inappropriate to consider the carbon trapped on the Al_2O_3 to result from volatilization on filter-collected carbon. Thus, the proposed FPC and LVFC samplers are probably ineffectual for their intended purposes.

In addition to the results given in Table 16, three alumina samples from each sampler were subjected to extraction with MeOH following

Ce WITH AND WITHOUT DENUDER (UG/M3) SAMPLER 1 = WITH DENUDER



gure 9.

Table 16. Atmospheric Results for FPC and LVFC Samplers ($\mu\text{g}/\text{m}^3$)

Period ^a	Sampler 1 (with Denuder)				Sampler 2 (No Denuder)			
	Filter		Al ₂ O ₃	Total	Filter		Al ₂ O ₃	Total
	$\text{C}_\text{o}-$	$\text{C}_\text{e}-$	$\text{C}_\text{o}-$	$\text{C}_\text{o}-$	$\text{C}_\text{o}-$	$\text{C}_\text{e}-$	$\text{C}_\text{o}-$	$\text{C}_\text{o}-$
26	16.5	5.6	11.2	27.7	16.9	5.4	14.4	28.3
27	10.5	5.6	16.6	27.1	9.0	4.6	3.3	12.3
36	14.9	5.6	8.1	23.0	15.6	5.8	5.2	20.8
37	9.1	4.2	3.1	12.2	10.4	4.3	2.5	12.9
46	18.2	5.4	5.5	23.7	19.1	5.5	7.1	26.2
47	7.5	3.7	7.5	15.0	7.5	3.8	b	-
56	19.6	5.1	5.8	25.4	16.8	5.2	13.8	30.6
57	7.6	3.7	9.1	16.7	7.4	3.5	2.9	10.3
66	16.3	3.7	3.4	19.7	16.8	3.5	3.9	20.7
67	11.6	2.6	4.2	15.8	11.9	2.6	4.2	16.1
76	16.9	2.6	4.0	20.9	17.6	2.9	2.3	19.9
77	7.5	2.9	8.8	16.3	8.1	2.8	4.4	12.5
86	11.9	4.4	3.2	15.1	15.6	4.3	5.5	21.1
87	7.8	2.7	2.3	10.1	10.1	2.8	7.7	17.8
96	12.8	3.3	19.4	32.2	14.2	3.9	11.1	25.3
97	10.1	3.3	8.7	18.8	11.4	3.4	5.5	16.9
106	15.1	5.4	7.4	22.5	15.9	5.6	4.5	20.4
107	10.2	4.5	6.0	16.2	11.2	4.7	6.3	17.5

a. The first digit indicates sampling day. The second day indicates the sampling period. Period 6 was 0800-2000 hours and period 7, 2000-0800 hours.

b. Bad data.

Figure 10.

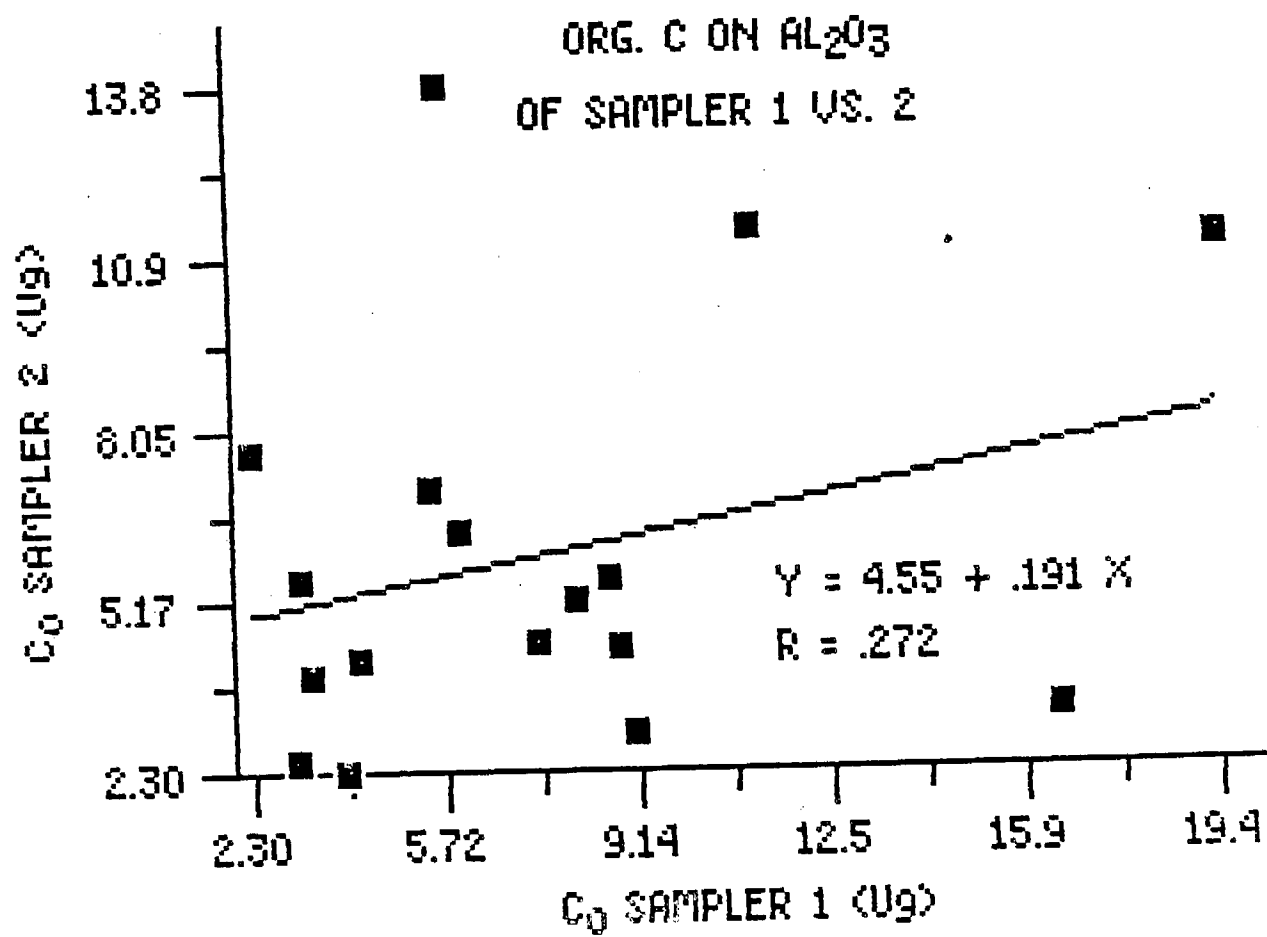
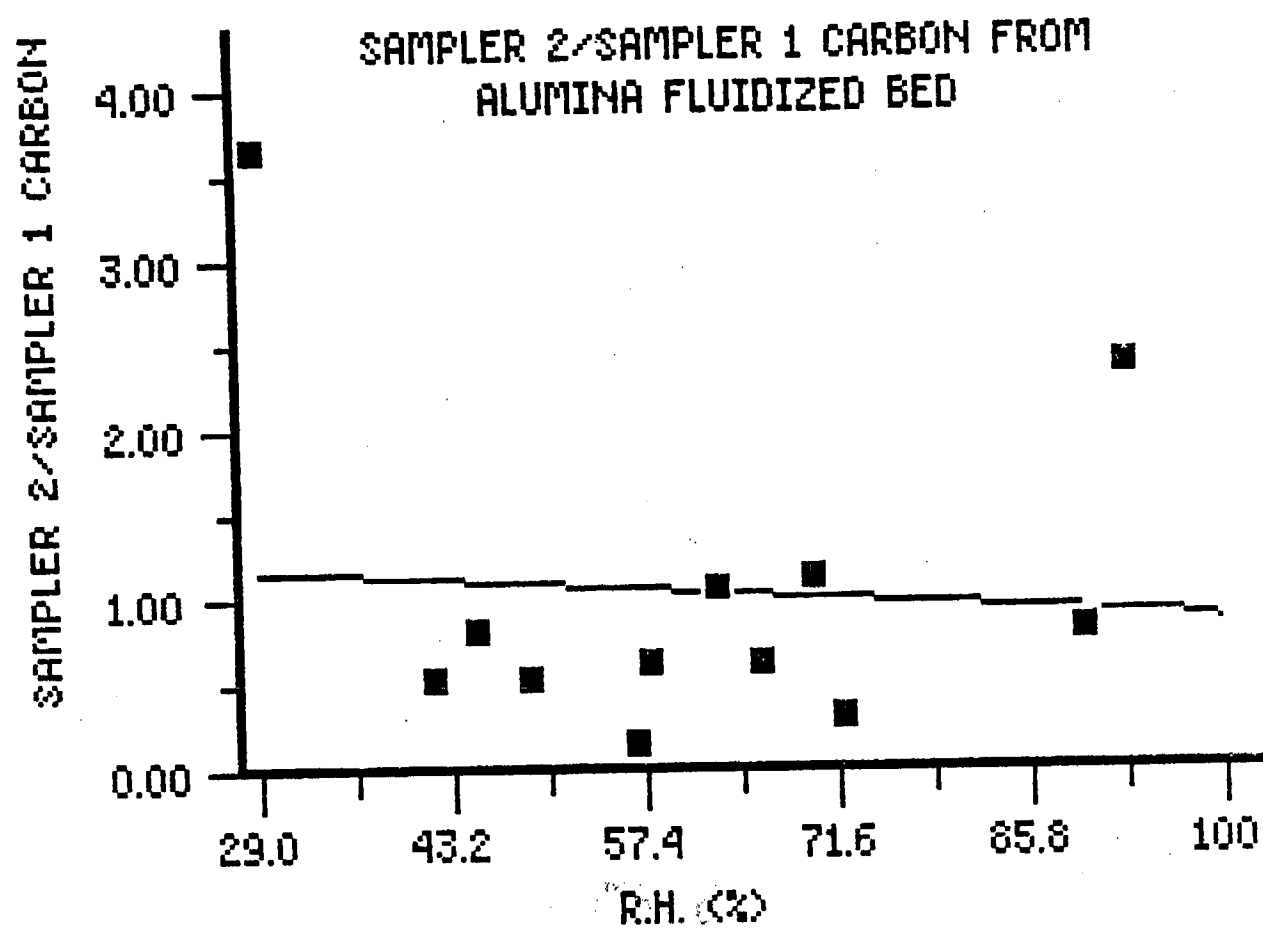


Figure 11.



extraction with MeCl_2 . Table 17 lists results for this subset of samples. For the sampler lacking a denuder, the organic carbon recovered with MeOH was about half that recovered with the less polar solvent. This contrasts with results for the sampler with denuder, for which carbon recovered with MeOH was <10% of that with MeCl_2 . These results, similar to earlier laboratory findings (Section IV D), suggest that the denuder was removing most of the more polar organics otherwise trapped on alumina. However, the absolute amount of carbon recovered with MeOH was insignificant in comparison to the organic carbon on the preceding filter. From these results, extraction of the remaining samples with MeOH in addition to MeCl_2 was not considered justified.

The present results with these samplers differ significantly from our previously published work. A comparison of these results may be useful. The preceding work was done at two urban and one background site located in a relatively clean, forested area. Sampling was done for 24-hour periods, rather than the 12-hr periods used in the present work. The filter medium employed was a prefired glass fiber type in place of the prefired, quartz filters used in the current work. The denuder was of the parallel tube design with alumina applied as a dusting onto an adhesive coating. The adhesive, rubber cement and silicone grease, may have contributed substantially to the sorption behavior of the denuder. A coating of silicone grease alone was subsequently shown to exhibit the same retention properties toward vapor phase model compounds (e.g. octadecane) as did tubes coated with the grease and a dusting of alumina. The parallel plate denuder in the present trials employed alumina without adhesive.

The denuder in the earlier study was shown to have relatively limited capacity compared to that in the present study for both hydrocarbons and more polar materials (e.g. dibutyl phthalate). Given the uncertainty of the vapor phase concentrations of the materials of interest, the difference in capacity is of uncertain significance.

C. The Influence of Face Velocity on Filter-Collected Carbon

The face velocity of the filters in samplers 1 and 2 were both 37 cm/sec, similar to that of the hi-vol sampler, sampler 3 (47 cm/sec). Accordingly, relatively similar recoveries of organic carbon would be expected. Table 18 compares sampler 1, 2, 3 (prefilter) and 4 (prefilter) organic carbon concentration values. For sampler 4, C_o values were, in general, below detection. Accordingly, Sampler 1 C_o values were used to obtain an improved estimate of organic carbon from sampler 4 with the equation: $C_o = C_t - C_e$. As expected, there is little difference among the results for samplers 1-3. However, sampler 4, which sampled at only 10 cm/sec, yielded C_o results which on average, were higher by, a factor of 1.5 relative to sampler 3 (Figure 12). Such higher results may reflect diminished volatilization losses at lower face velocity, enhanced sorption of initially gas-phase materials at low face velocity, and/or the fact that sorption of initially gas-phase

Table 17. Recovery of Citrus College Atmospheric Carbon from Filters and Al_2O_3 by MeCl_2 Extractions Followed by Extraction with MeOH

Sampling Period ^a	Quartz Filter C		Al ₂ O ₃ Fluidized Bed			
	<u>μg</u>	<u>μg/m³</u>	<u>MeCl₂</u>		<u>MeOH</u>	
			<u>μgC</u>	<u>μg/m³</u>	<u>μgC</u>	<u>μg/m³</u>
Sampler 1 (with Denuder)						
36	222	14.9	121	8.1	6.3	0.4
47	103	7.52	112	8.2	2.0	0.1
66	230	16.3	47.4	3.4	1.1	0.1
Sampler 2 (without Denuder)						
36	224	15.6	74.6	5.2	31.5	2.2
47	102	7.5	b	b	9.6	0.7
66	237	16.8	55.6	3.9	29.6	2.1

a. The first digit indicates sampling day. The second day indicates the sampling period. Period 6 was 0800-2000 hours and period 7, 2000-0800 hours.

b. Bad data.

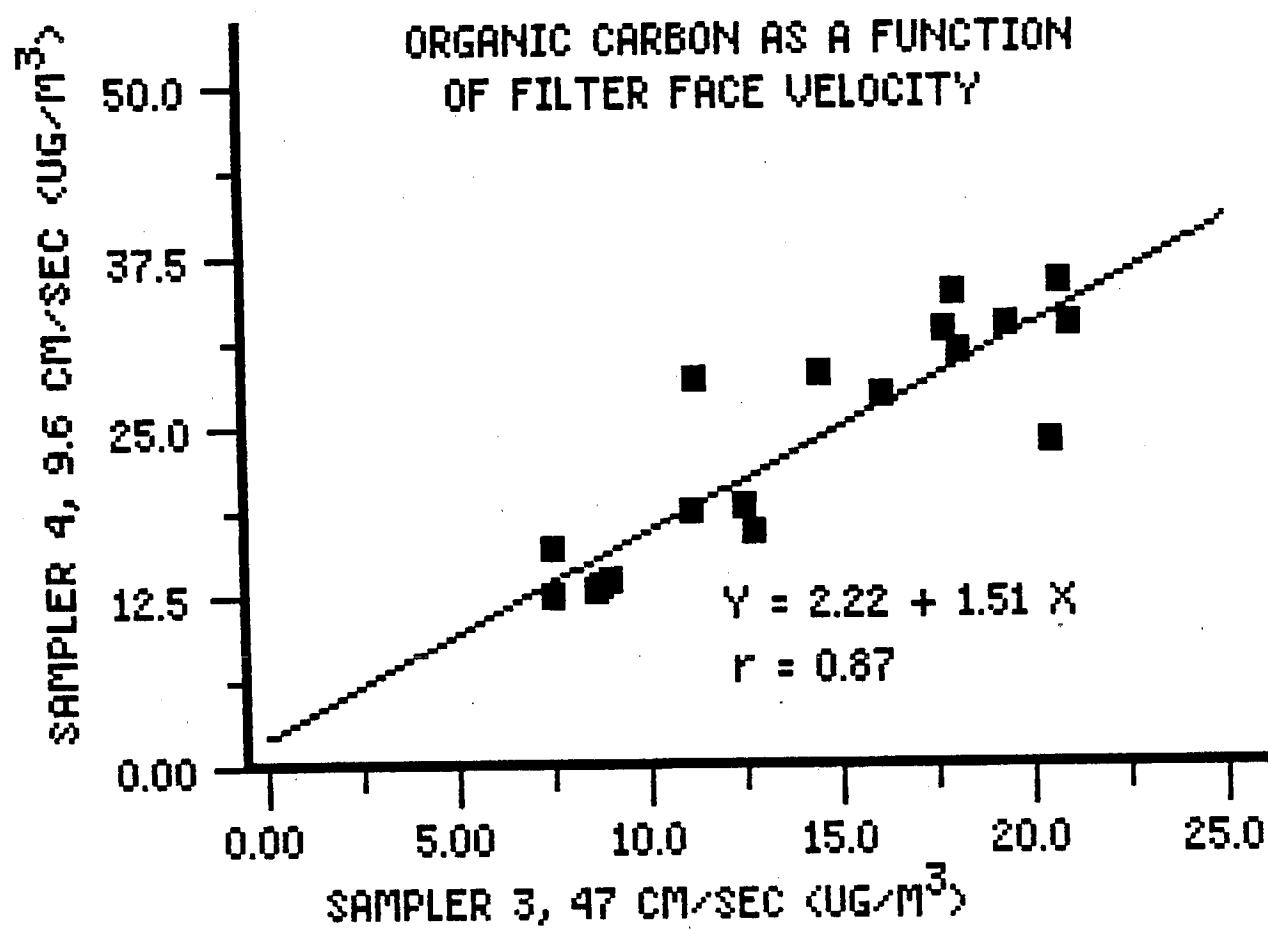
Table 18. Influence of Face Velocity on Filter-Collected Organic Carbon ($\mu\text{g}/\text{m}^3$)^a

Period	Sampler			
	<u>1 (37 cm/sec)</u>	<u>2 (37 cm/sec)</u>	<u>3 (47 cm/sec)^b</u>	<u>4 (9.6 cm/sec)^b</u>
26	16.5	16.9	18.2	30.4
27	10.5	9.01	8.8	12.9
36	14.9	15.6	17.8	31.9
37	9.13	10.4	8.74	12.6
46	18.2	19.1	20.8	35.5
47	7.52	7.53	7.54	15.8
56	19.6	16.8	19.4	32.2
57	7.58	7.53	7.57	12.2
66	16.3	16.8	21.0	32.1
67	11.6	11.9	12.5	19.1
76	16.9	17.6	14.6	28.6
77	7.5	8.12	9.03	13.6
86	11.9	15.6	18.0	34.5
87	7.8	10.1	11.3	28.2
96	12.8	14.2	16.2	27.2
97	10.1	11.4	11.2	18.5
106	15.1	15.9	20.6	23.8
107	10.2	11.2	12.8	17.1

a. Results for samplers 3 and 4 averaged to permit comparison with the 12 hour values from samplers 1 and 2.

b. Prefilter.

Figure 12



materials on the filter occurs for a greater proportion of the sampling period because of the much lower air volume sampled at low face velocity.

In contrast to organic carbon, no difference in elemental carbon levels would be expected because of the influence of face velocity. An evaluation of the influence of face velocity on measured C_e was hampered by the low levels of carbon collected at 8 cm/sec in short term samples. Only five sampling periods provided C_e levels above the lower limit for reliable quantitation with sampler 4 prefilterers. For these five periods, the correlation with sampler 3 (47 cm/sec) prefilter results for C_e are expressed as: Sampler 4 $C_e = 1.47 + 0.61$ Sampler 3 C_e , $r=0.985$. On average, sampler 4 C_e values were lower by 19%. This relatively small difference can be attributed to analytical error rather than to a face velocity effect.

D. Tandem Filter Sampling for Organic Carbon

Tandem filter sampling with Pallflex QAO filters was done in parallel with two samplers at face velocity 10 and 47 cm/sec. Of interest was to compare the proportion of the total carbon retained on the second filter at the two face velocities. Figures 13 and 14 are scatter diagrams for the after-filter against prefilter organic carbon results for the two samplers, expressed in $\mu\text{g C/cm}^2$. For sampler 3 (47 cm/sec), prefilter results ranged from 5 to 18 $\mu\text{g/cm}^2$ and after-filters, from 1 to 4.5 $\mu\text{g/cm}^2$. The results show relatively good positive correlation, with about 20% of the recovered carbon on the after-filter.

With sampler 4 (10 cm/sec), the loadings, in $\mu\text{g/cm}^2$, were lower for both prefilterers and after-filters compared to sampler 3. The correlation between sampler 4 carbon data for the two filter types was poor. However, on average, the after-filter C represented about 20% of the total recovered carbon, similar to results with sampler 3. The maximum loading observed with the after-filter was about equal to that for sampler 3 (i.e. 4.5 $\mu\text{g/cm}^2$), perhaps indicating saturation conditions for vapor phase C on the quartz filter.

Figure 15 compares loadings on the after-filters of the two samplers, in $\mu\text{g/cm}^2$. Sampler 3 after-filter loadings were 2 or 3 times those of sampler 4, although the flow per unit area for sampler 3 was higher by a factor of nearly 5. Thus the after-filter of sampler 4 retained carbon more efficiently. A more direct indication of this is the determination of loading in $\mu\text{g/m}^3$. Figure 16 compares sampler 3 and 4 after-filter C concentrations. Sampler 4 indicates about twice the C concentration of sampler 3.

If the carbon on the after-filter is assumed to result only from the retention of a small fraction of the vapor phase organic materials passing through both filters, then these results can be used to estimate particle phase carbon on the front filter. This follows since similar retention of such vapor-phase materials on both filters would be expected (at least while the prefilter

Figure 13.

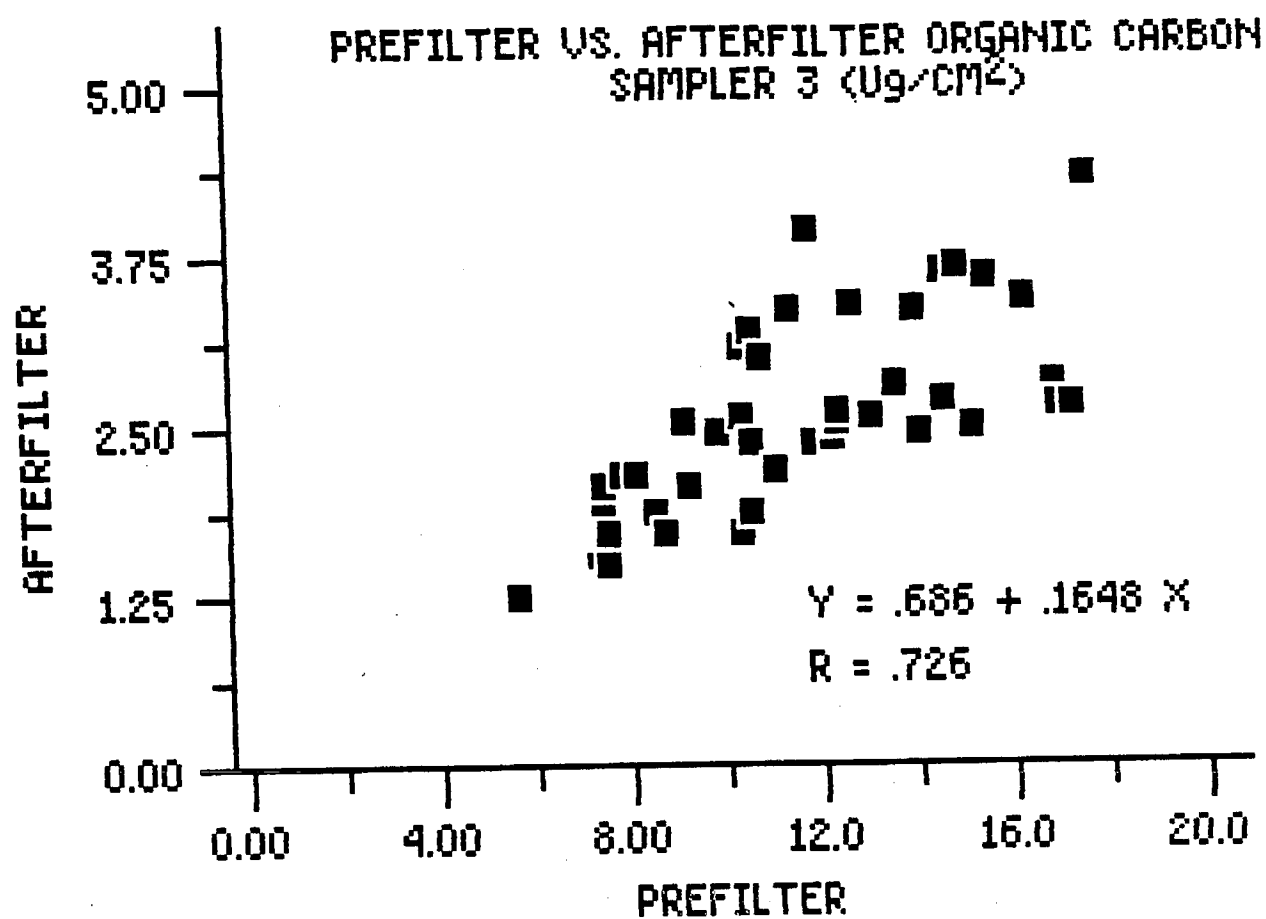


Figure 14.

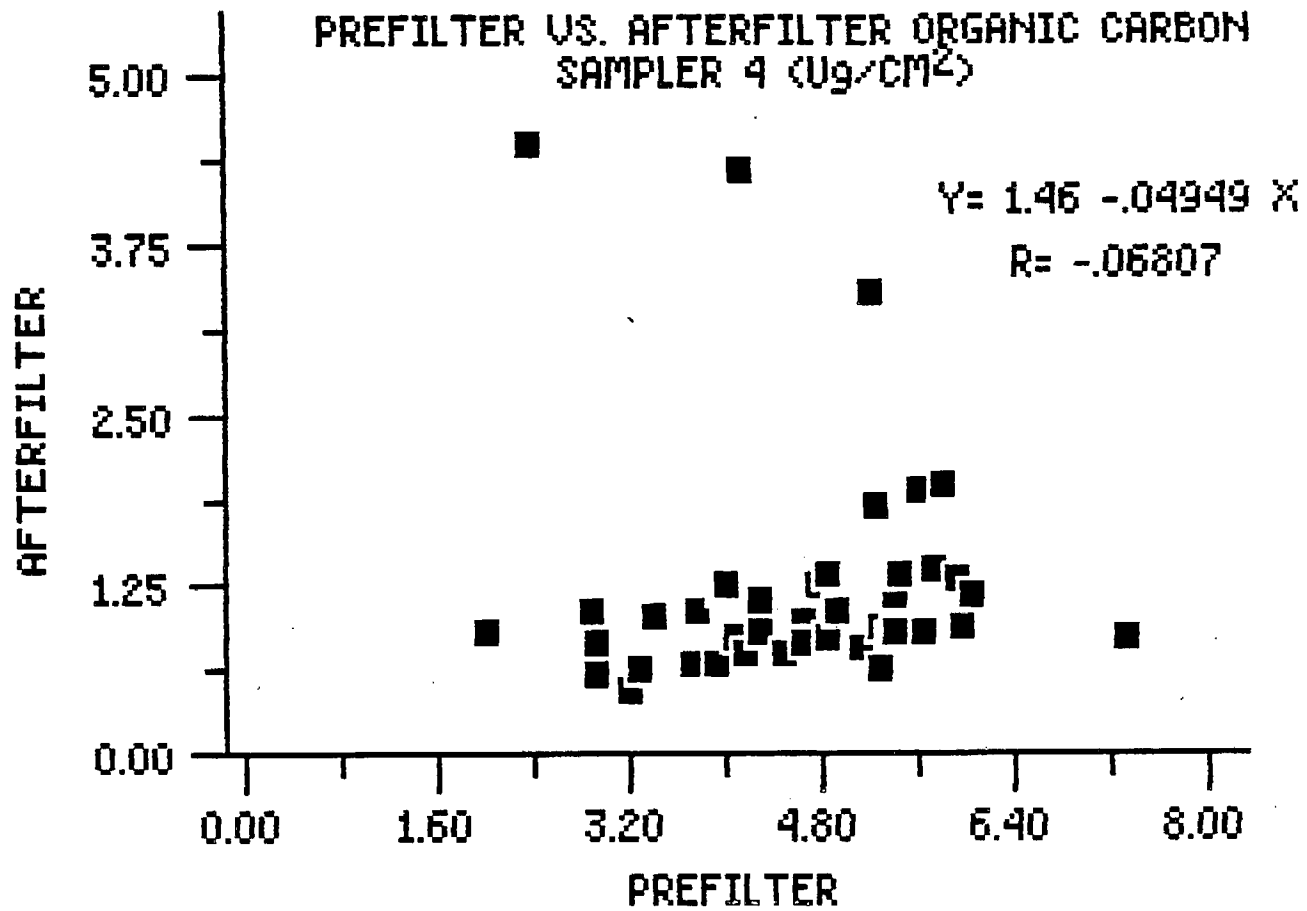


Figure 15.

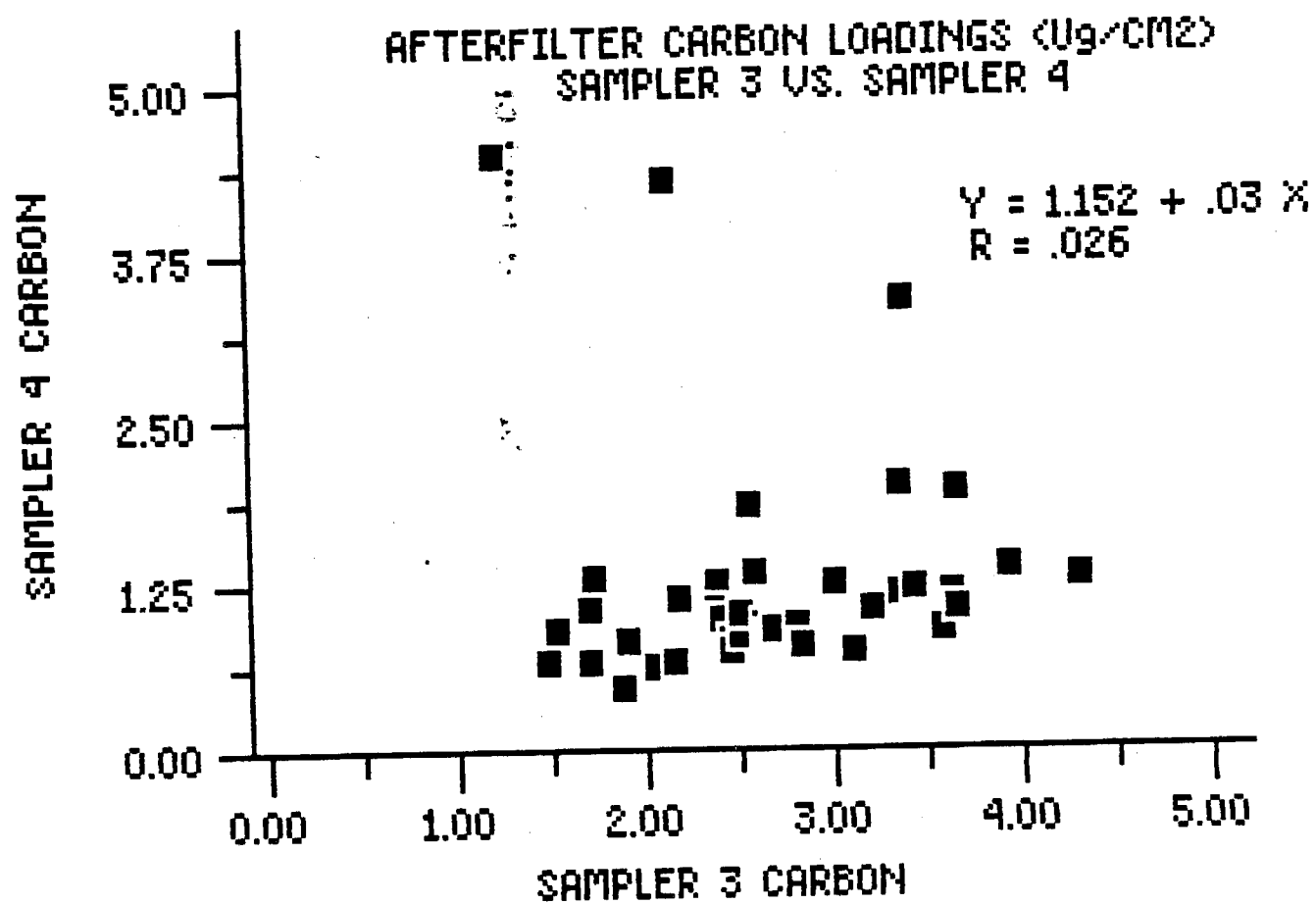
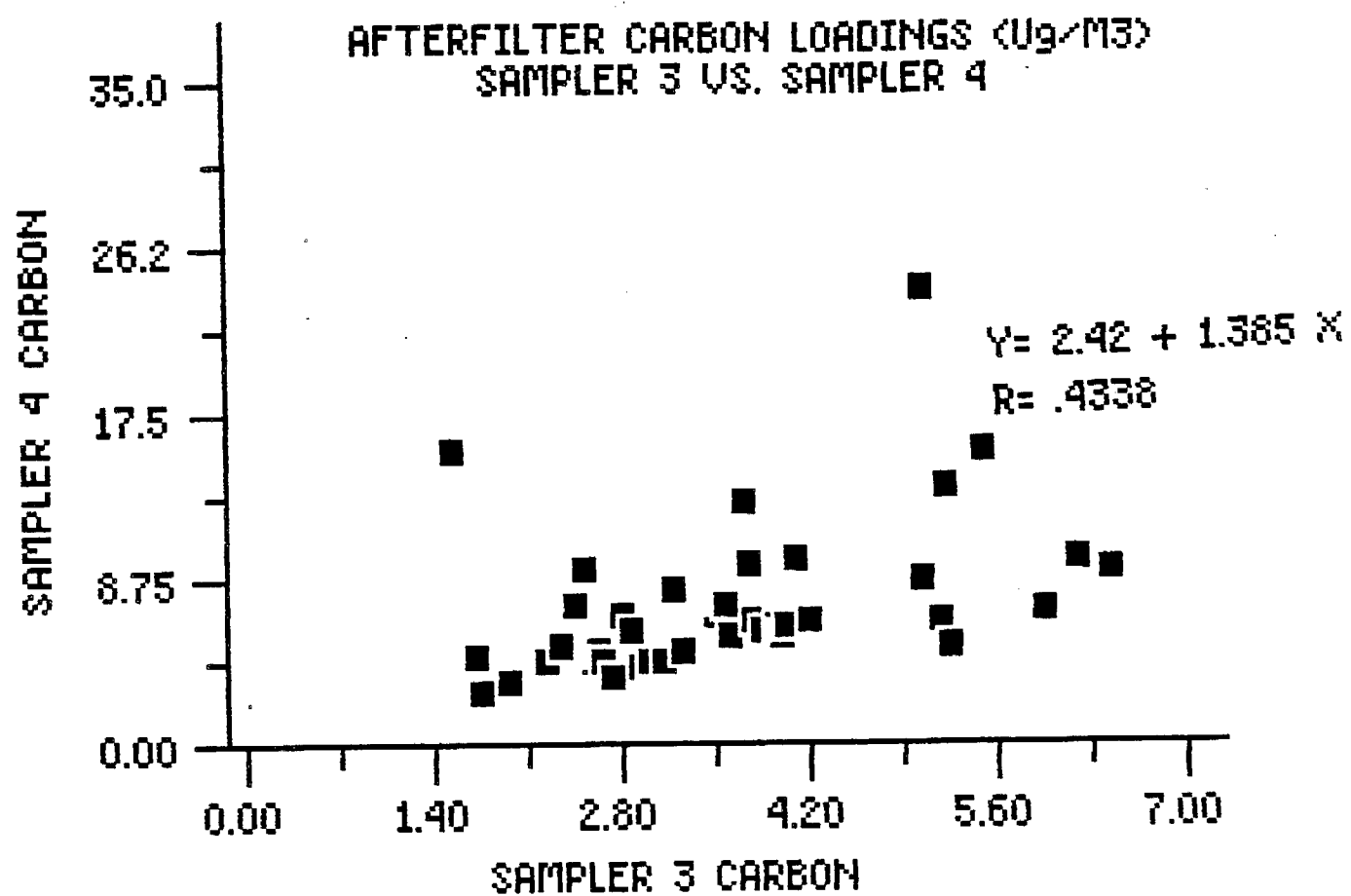


Figure 16.



remained lightly loaded with particulate matter). Table 19 lists such corrected results for samplers 3 and 4. The data sets are compared in Figure 17, indicating that the dependence of measured particulate organic carbon on face velocity (Figure 10), is not eliminated by such a correction strategy. This is consistent with relatively efficient retention of vapor phase organic compounds on quartz filters. Such retention would substantially lower the concentrations of these materials reaching the after-filter, making the subtraction strategy ineffective.

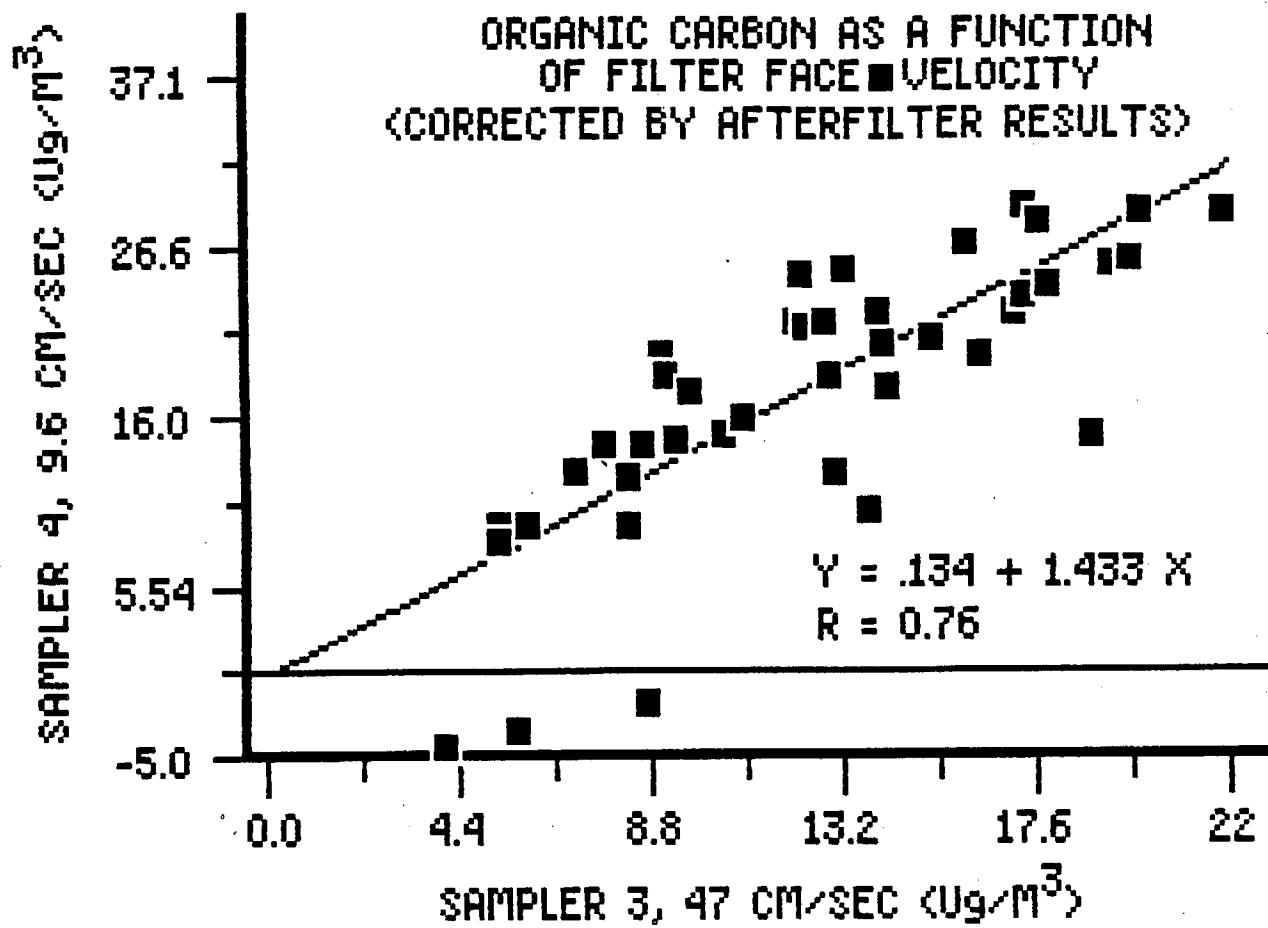
Table 19

PARTICULATE ORGANIC CARBON ESTIMATED FROM TANDEM
FILTER SAMPLES (ug/M3)

sampling period	sampler #3	sampler #4
21	13.75	10.41
22	17.37	23.76
23	9.38	14.84
24	8.53	14.67
25	5.34	9.45
31	12.35	21.83
32	14.25	18.19
33	15.26	20.89
34	8.29	9.36
35	5.97	9.36
41	12.27	24.99
42	16.32	19.93
43	17.31	29.26
44	9.04	19.99
45	4.11	-4.43
51	13.3	25.21
52	19.76	26.11
53	12.96	18.64
54	6.6	-18.66*
55	5.35	8.63
61	12.18	21.9
62	17.64	28.16
63	19.93	28.89
64	9.74	17.63
65	10.55	14.95
71	19.34	25.57
72	21.87	28.84
73	14.01	22.66
74	8.78	-1.83
75	5.76	-3.46
81	14.13	37.17
82	17.09	22.73
83	12.8	22.14
84	10.86	44.9*
85	7.13	12.72
91	14.18	20.74
92	15.99	26.97
93	7.8	14.32
94	8.27	12.45
95	8.66	14.3
101	17.9	24.18
102	18.86	15.1
103	10.91	16.02
104	9.13	18.75
105	13.06	12.8

* Results probably in error.

Figure 17.



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